9.16
The Groundwater Geochemistry of Waste Disposal Facilities

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9.16.1 INTRODUCTION

Landfills of solid waste are abundant sources of groundwater pollution. The potential for generating strongly contaminated leachate from landfill waste is very substantial. Even for small landfills the timescale can be measured in decades or centuries. This indicates that waste dumps with no measures to control leachate entrance into the groundwater may constitute a source of groundwater contamination long after dumping has ceased. In addition to these dumps, engineered landfills with liners and leachate collection systems may *also* constitute a source of groundwater contamination due to inadequate design, construction, and maintenance, resulting in the leakage of leachate.

Landfills may pose several environmental problems (explosion hazards, vegetation damage, dust and air emissions, etc.), but groundwater pollution by leachate is considered to be the most important one and the focus of this chapter. Landfills differ significantly depending on

the waste they receive: mineral waste landfills for combustion ashes, hazardous waste landfills, specific industrial landfills serving a single industry, or municipal waste landfills receiving a mixture of municipal waste, construction, and demolition waste, waste from small industries and minor quantities of hazardous waste. The latter type of landfill (termed "old landfills" in this chapter) is very common all over the world. Municipal landfills are characterized by a high content of organic waste that affects the biogeochemical processes in the landfill body and the generation of strongly anaerobic leachate with a high content of dissolved organic carbon, salts, ammonium, and organic compounds and metals released from the waste.

This chapter describes the biogeochemistry of a landfill leachate plume as it emerges from the bottom of a landfill and migrates in an aquifer. The landfill hydrology, source composition, and spreading of contaminants are described in introductory sections. The focus of this chapter is on investigating the biogeochemical processes associated with the natural attenuation of organic contaminants in a leachate plume. Studies have shown that microbial processes and geochemical conditions change over time and distance in contaminant plumes, resulting in different rates of degradation (biotic and abiotic). The availability of electron acceptors, such as iron oxides or dissolved sulfate, is an important factor for evaluating the efficacy and sustainability of natural attenuation as a remedy for leachate plumes. Understanding the complex environments developing in leachate plumes is important in assessing the risk to groundwater resources and for developing cost-effective remediation strategies.

9.16.2 SOURCE AND LEACHATE COMPOSITION

Landfills as pollution sources have three key characteristics:

- they are large often heterogeneous sources both in volume and area;
- they host a mixture of inorganic and organic pollutants; and
- they have an expected pollution potential lasting for decades to centuries.

The area of landfills typically ranges from a few hectares up to more than 50 ha (Christensen *et al.*, 2001). The amount of waste can be enormous ($1 \times 10^5 - 5 \times 10^6$ m^3).

The presence of a mixture of contaminants in the landfill body affects the overall behavior of the pollution plume, and the interaction between various contaminants. The natural setting of landfills is crucial for understanding the biogeochemistry of landfill leachate plumes.

In comparison with other groundwater pollution sources, the complexity of the source means that many different compounds (inorganic and organic) and processes (geochemical and microbial) will be interacting in a landfill leachate plume.

Landfill leachate is generated by excess rainwater percolating through landfilled waste layers. Combined physical, chemical, and microbial processes in the waste transfer pollutants from the waste material to the percolating water. Leachates from common types of landfill that receive a mixture of municipal, commercial, and mixed industrial waste, but excluding significant amounts of concentrated specific chemical waste, may be characterized as a water-based solution containing four groups of pollutants (Christensen *et al.*, 1994).

- Dissolved organic matter, expressed as chemical oxygen demand (COD) or total organic carbon (TOC), including methane, volatile fatty acids (in particular in the acid phase of the waste stabilization; Christensen and Kjeldsen (1989), and more refractory compounds, e.g., fulvic-like and humic-like compounds.
- Inorganic macrocomponents: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), ammonium (NH_4^+), iron (Fe^{2+}), manganese (Mn^{2+}), chloride (Cl^-), sulfate (SO_4^{2+}), and bicarbonate (HCO_3^-).
- Heavy metals: cadmium (Cd^{2+}), chromium (Cr^{3+}), copper (Cu^{2+}), lead (Pb^{2+}), nickel (Ni^{2+}), and zinc (Zn^{2+}).
- Xenobiotic organic compounds (XOCs) originating from household or industrial chemicals and present in relatively low concentrations in the leachate (usually less than 1 mg L^{-1} of individual compounds). These compounds include, among others, a variety of aromatic hydrocarbons, phenols, chlorinated aliphatic hydrocarbons, and pesticides.

Other compounds may be found in leachate from landfills, e.g., borate, sulfide, arsenate, selenate, barium, lithium, mercury, and cobalt. In general, however, these components are not often measured; when they are measured, they are usually present in very low concentrations and are considered only of secondary importance.

Leachate composition varies significantly among landfills, depending on waste composition, waste age, and landfill technology. The waste can be divided into three main groups: household waste, demolition waste, and chemical and hazardous waste.

In nonengineered landfills, the different types of waste are randomly distributed at the site. Historical records are often nonexistent, and investigations are often based on interviews, aerial photos (over time), and excavations. Experiences from Danish sites have shown that combining these methods is an efficient way to develop a good

description of the composition of the landfilled waste (Kjeldsen, 1993; Kjeldsen *et al.*, 1998a,b).

Investigations of leachate composition have often been based on only one or a few leachate samples from each landfill. In the context of groundwater pollution, the spatial distribution of the leachate quality must be appreciated. This requires a large number of sampling points (Kjeldsen *et al.*, 1998a). For instance, significant spatial variability in leachate concentrations was observed in wells at the 10 ha Grindsted Landfill (DK) (Kjeldsen *et al.*, 1998a). Very low concentrations of almost all parameters (including XOCs) were found in areas covering ~60–70% of the landfill. A "hot spot," occupying ~10% of the landfill area, was found with concentrations 20–1,000 times higher than in the low-concentration area. Especially for large landfills, information on spatial variability in leachate concentrations is very important as a basis for locating the main sources of the groundwater pollution plume and for selecting cost-effective remedial actions.

Table 1 presents ranges of common leachate parameters compiled from data reported in the literature. The table is based mainly on data from newer landfills (leachate less than 25 yr old). Data from older uncontrolled landfills may exhibit lower values than the minimum values given in the table (Assmuth and Strandberg, 1993; Kjeldsen and Christophersen, 2001). Landfill leachates may contain very high concentrations of dissolved organic matter and inorganic macrocomponents. The concentrations of these components may typically be up to a factor of 10–500 higher than groundwater concentrations in pristine aquifers; however, significant variability is common.

Leachate also contains a broad range of XOCs (Table 2). Since the composition of chemical

Table 1 Composition of landfill leachate. Values in mg L^{-1} unless otherwise stated.

Parameter	Range
pH (no unit)	4.5–9
Spec. cond. (μS cm^{-1})	2,500–35,000
Total solids	2,000–60,000
Organic matter	
TOC	30–29,000
Biological oxygen demand (BOD$_5$)	20–57,000
COD	140–152,000
BOD$_5$/COD (ratio)	0.02–0.80
Organic nitrogen	14–2,500
Inorganic macrocomponents	
Total phosphorus	0.1–23
Chloride	150–4,500
Sulphate	8–7,750
Hydrogencarbonate	610–7,320
Sodium	70–7,700
Potassium	50–3,700
Ammonium-N	50–2,200
Calcium	10–7,200
Magnesium	30–15,000
Iron	3–5,500
Manganese	0.03–1,400
Heavy metals	
Arsenic	0.01–1
Cadmium	0.0001–0.4
Chromium	0.02–1.5
Cobalt	0.005–1.5
Copper	0.005–10
Lead	0.001–5
Mercury	0.00005–0.16
Nickel	0.015–13
Zinc	0.03–1,000

Source: Kjeldsen *et al.* (2002).

Table 2 The most frequently observed XOCs in landfill leachates. Only pollutants that have been observed in more than three independent investigations are included.

Compound	Range (μg L^{-1})
Aromatic hydrocarbons	
Benzene	0.2–1,630
Toluene	1–12,300
Xylenes	0.8–3,500
Ethylbenzene	0.2–2,300
Trimethylbenzenes	0.3–250
Naphthalene	0.1–260
Halogenated hydrocarbons	
Chlorobenzene	0.1–110
1,2-Dichlorobenzene	0.1–32
1,4-Dichlorobenzene	0.1–16
1,1-Dichloroethane	0.6–46
1,2-Dichloroethane	<6
1,1,1-Trichloroethane	0.1–3,810
Trichloroethylene	0.05–750
Tetrachloroethylene	0.01–250
Dichloromethane	1.0–827
Trichloromethane	1.0–70
Phenols	
Phenol	0.6–1,200
Cresols	1–2,100
Pesticides	
Mecoprop[a]	0.38–150
Phtalates	
Diethylphthalate	10–660
Di-(2-ethylexyl)phtalate	0.6–240
Di-*n*-butylphthalate	0.1–70
Butylbenzyl phtalate	0.2–8
Phosphonates	
Tri-*n*-butylphosphate	1.2–360
Miscellaneous	
Acetone	6–4,400
Camphor[b]	20–260
Fenchone	7–80
Tetrahydrofuran	9–430

Source: Kjeldsen *et al.* (2002).
[a] 2-(2-methyl-4-chlorophenoxy) propionic acid (MCPP).
[b] 1,7,7-trimethyl-bicyclo(-bicyclo[2.2.1]-heptane-2-one.

wastes is highly variable, the compounds identified and their concentration ranges are difficult to summarize in general terms. An important subgroup is that of volatile organic compounds (VOCs); these are organic compounds that tend to vaporize at room temperature and pressure. Typically VOCs are an important component of the compounds in gasoline, lubricants, and solvents. Some VOCs are highly toxic and/or carcinogenic. Aromatic hydrocarbons and chlorinated aliphatic compounds are the most frequently found compounds in landfill leachate. They are also the most common compounds included in analytical programs. Phenols, pharmaceuticals, and pesticides have been found as well, and other ionic or polar compounds (e.g., phthalates and aromatic sulfonates) have been identified in more recent investigations (e.g., Schwarzbauer et al., 2002; Paxeus, 2000).

Several parameters change dramatically as the organic waste in the landfill degrades. During the initial fermentation (acid phase), leachates may have low pH values and high concentrations of many compounds, in particular high concentrations of easily degradable organic compounds such as volatile fatty acids. Later, when the fermentation products are converted effectively to methane and carbon dioxide (methane phase), the pH increases and the degradability of the organic carbon in the leachate decreases. A detailed discussion of the phases which landfills experience is given in Kjeldsen et al. (2002).

The data in Tables 1 and 2 are based on leachates from landfills that are younger than 25 yr. The values are difficult to extrapolate beyond the first 25 years of a landfill's life. Belevi and Baccini (1992) estimated by using leaching tests on municipal solid waste that leachate from landfills contains significant concentrations of several compounds for centuries. The leachates contain nitrogen and organic carbon in significant concentrations for several centuries as discussed in detail by Kjeldsen et al. (2002).

In summary, leachates contain a variety of compounds (dissolved organic matter, inorganic compounds, heavy metals, and XOCs), due to the mixed nature of the waste in landfills. The spatial variability of the leachate quality is significant, and this can affect the leaching pattern from the landfill and the resulting plumes. A landfill should be seen as a complex source, which is expected to last for decades or even centuries.

9.16.3 SPREADING OF POLLUTANTS IN GROUNDWATER

All compounds in leachate entering an aquifer will be subject to advection and dispersion (dilution) as the leachate mixes with groundwater (Freeze and Cherry, 1979). For nonreactive components, of which chloride is the dominant component, dilution is the only attenuation mechanism. Dilution is the interaction of the leachate flow in the aquifer with the flow of groundwater. Leachate migration should be seen in terms of a three-dimensional plume developing in a three-dimensional geological structure, where gradients, permeabilities, and physical boundaries (geological strata, infiltration, rivers, abstraction wells, etc.) determine the position and migration velocity of the plume. Dilution is governed by macroscopic dispersion and molecular diffusion, but can also be affected by local vertical gradients, leachate density, and, to some extent, viscosity.

Dispersion is the mathematical term in the solute transport equation (Freeze and Cherry, 1979) accounting for dilution or mixing according to concentration gradients. The dispersivity has a longitudinal component (in the flow direction), a vertical component, and a horizontal, transverse component. The longitudinal dispersivity is important only for concentrations at the front of leachate plumes. Of greater interest is the magnitude of the transverse dispersivities, which govern the transverse spreading of the plume. Data from field experiments (review by Gelhar et al. (1992), Jensen et al. (1993), Petersen (2000), and Adams and Gelhar (1992)) showed small transverse dispersivities (from millimeters to a few centimeters) indicating limited transverse spreading of pollution plumes. Unfortunately, field data showing detailed horizontal delineations of landfill leachate plumes have not been presented since the early investigations of the Borden Landfill (Figure 1). The review of Gelhar et al. (1992) also indicates that vertical transverse dispersivities are extremely small, which implies very limited vertical mixing due to dispersion alone. This has been confirmed in a number of landfill studies (e.g., Nicholson et al., 1983; Barker et al., 1986; Lyngkilde and Christensen, 1992b; Bjerg et al., 1995), where steep vertical concentration gradients of chloride have been observed (Figures 1 and 2).

The flow of leachate may, as mentioned, differ physically from that of groundwater at least with respect to the following three aspects.

Local water table gradients below and around the landfill will most likely differ from the general gradients, because the landfill will usually have a different hydrology/hydrogeology compared to the surrounding area. Local water table mounds have been observed at the Borden Landfill (CAN) (MacFarlane et al., 1983), Vejen Landfill (DK) (Kjeldsen, 1993), the Noordwijk Landfill (NL) (van Duijvenbooden and Kooper, 1981), and at the Grindsted Landfill (DK) (Kjeldsen et al., 1998b). The reasons for water mounds are not fully understood (see later discussion in Section 9.16.7.1).
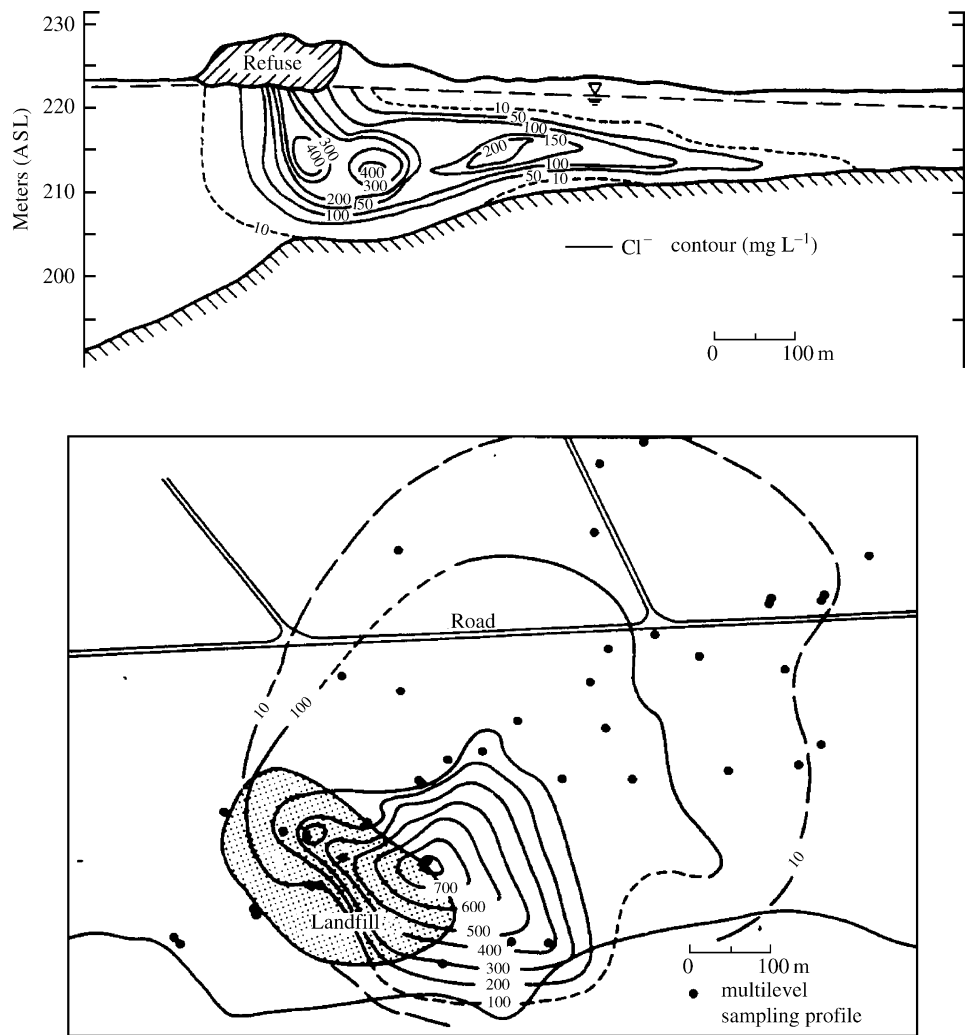
Figure 1 Horizontal and vertical transect contours of Cl$^-$ (mg L^{-1}) in the Borden Landfill (CAN) (source MacFarlane *et al.*, 1983).
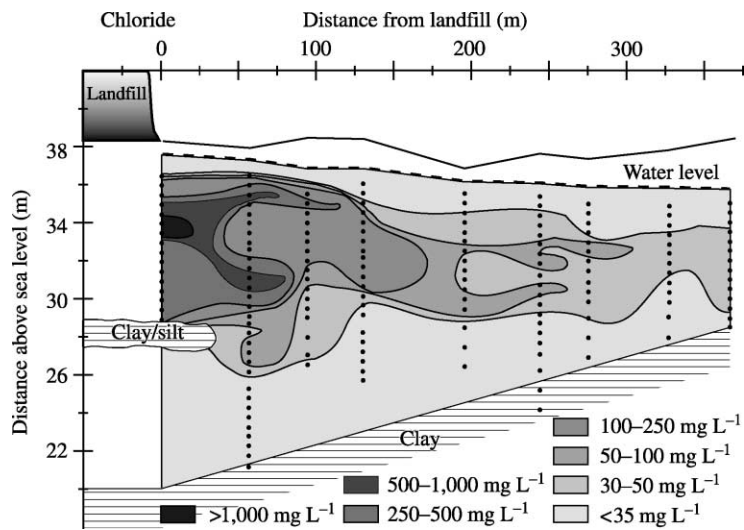
Figure 2 Vertical transect contours of Cl$^-$ (mg L^{-1}) in the Vejen Landfill (DK) (source Lyngkilde and Christensen, 1992b).

Local mounding effects are enhanced lateral spreading of the leachate plume, and to downward directed hydraulic gradients in the groundwater zone beneath the landfill. The latter can cause an unexpected spreading pattern despite homogeneous aquifer conditions and limited density difference between leachate and the ambient groundwater. The enhanced lateral spreading of the plume may increase the volume of contaminated groundwater and its spatial extent, but provides increased dilution of contaminants.

The viscosity of the leachate may differ from that of the groundwater. A higher viscosity should lead to lower flow velocities, which could influence the dilution of the leachate plume; however, actual field evidence is scarce (Christensen *et al.*, 2001).

The density of the leachate is a function of the temperature and the concentration of dissolved solids. Leachate with a total dissolved solid concentration of 2×10^4 mg L^{-1} is not uncommon (see Table 1); the density of such a leachate is >1% higher than the groundwater density. Density differences may significantly affect the vertical positioning of the plume just below the landfill. Field observations on the downward movement of the plume are often difficult to separate from the effect of local water table mounds (Christensen *et al.*, 2001). A better understanding of the effects of higher leachate densities in field situations is needed. Density effects could be the major cause of vertical leachate spreading in aquifers since "normal" vertical dispersion is usually very small.

In summary, transport and spreading of dissolved landfill leachate pollutants in aquifers are governed by advection/dispersion. The local hydrogeology at the site in terms of water table mounds and seasonal variation in flow field may enhance the spreading horizontally and vertically. Density effects due to high concentrations of inorganic compounds may increase vertical transport, but the understanding of density transport in leachate plumes is poor. Density transport is likely to be most important close to landfills but less so as dilution of the plume increases.

9.16.4 BIOGEOCHEMISTRY OF LANDFILL LEACHATE PLUMES

9.16.4.1 Redox Environments and Redox Buffering

The entry of strongly reduced landfill leachate into a pristine, often oxidized, aquifer, leads to the creation of very complex redox environments. Important processes include organic matter biodegradation, biotic and abiotic redox processes, dissolution/precipitation of minerals, complexation, ion exchange, and sorption. The resulting redox environments strongly influence both the inorganic and organic biogeochemistry of the aquifer, and create the chemical framework for understanding the attenuation processes in the plume.

Characterization of redox environments in pollution plumes has been reviewed by Christensen *et al.* (2000b). A range of different approaches have been used in addressing redox conditions in pollution plumes:

- redox potential,
- redox-sensitive compounds in groundwater samples,
- hydrogen concentrations in groundwater,
- concentrations of volatile fatty acids,
- sediment characteristics, and
- microbial tools.

However, it should be noted that the approaches are not standard, and the value of each approach is still a matter of debate (Christensen *et al.*, 2000b). In addition, the redox conditions in contaminant plumes are not only spatially variable but also temporally variable (McGuire *et al.*, 2000).

In the following, we discuss the redox environments observed in landfill leachate plumes, based on the simplified presentation of redox conditions as given in Figure 3. Later in this chapter it is shown for two case histories (Sections 9.16.5 and 9.16.6) that the actual redox conditions may be somewhat more complex. In an aquifer with a continuous leachate release, a methanogenic zone evolves close to the landfill. Within this zone and downgradient from it, sulfate reduction may take place. Iron reduction takes place further downgradient, where the conditions are less reducing. Zones of manganese and nitrate reduction have been observed, sometimes overlapping the iron-reducing zone. Finally, aerobic conditions may exist in the outskirts of the reduced plume, if the pristine aquifer is oxidized and contains significant amounts of dissolved oxygen (>1 mg L^{-1}).

As illustrated in Figure 3, the content of reduced species (organic matter and ammonium) in groundwater decreases along the flow lines. The redox potential increases with distance. Close to the landfill, dissolved electron acceptors such as oxygen, nitrate, and sulfate are depleted or lowered in concentration. Sulfide may be present due to sulfate-reducing processes. At some distance from the source, the content of reduced dissolved species such as sulfide, ferrous iron, and manganese peaks as a result of redox processes. The composition of the minerals in the aquifer changes with distance, as discussed below. The pollutants leaving the landfill will, unless they are removed from the water, migrate through a series of redox zones, and over time migrate into more oxidizing environments.
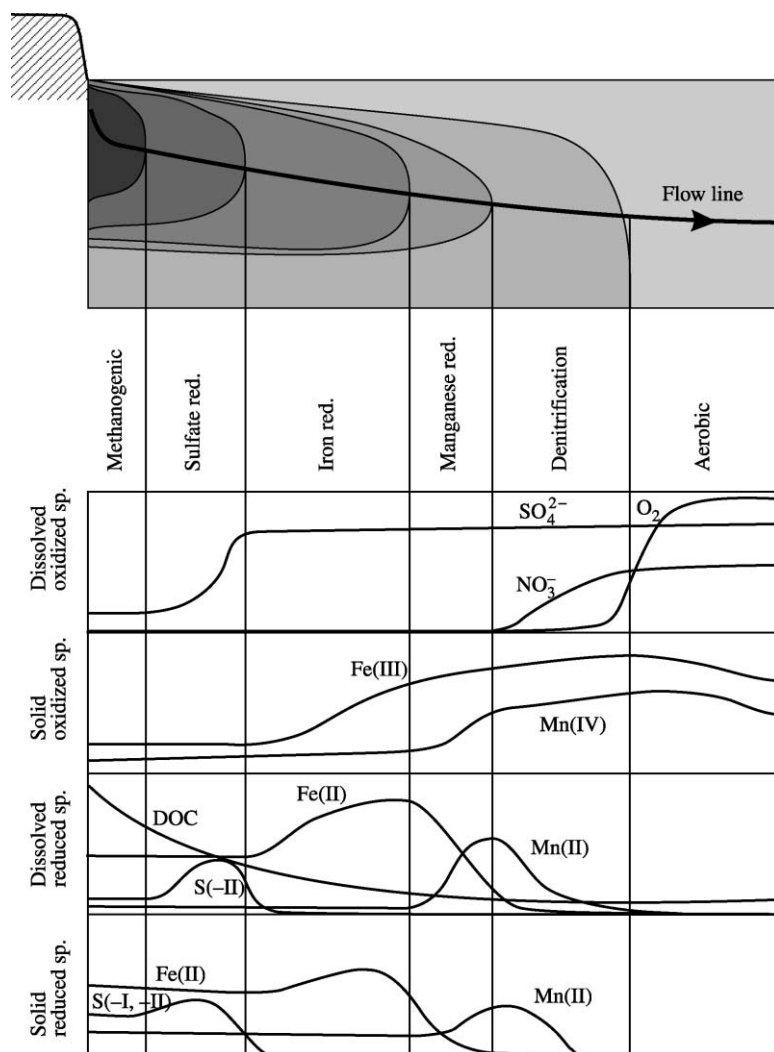
Figure 3 Schematic redox zonation in an originally aerobic aquifer downgradient from a landfill, and the distribution of redox-sensitive species along a streamline in the plume. The axes are not to scale (source Christensen *et al.*, 2001).

Leachate from landfills typically is strongly reduced, rich in organic matter and ammonium, and may be seen as infiltrating water with a great capacity for donating electrons (reduction capacity) during redox reactions. The produced electrons must be accepted by dissolved or solid aquifer electron acceptors. The capacity of the aquifer to accept electrons is called the oxidation capacity (OXC; Scott and Morgan, 1990; Heron *et al.*, 1994a).

The set of reactions that creates the complex redox environments of landfill leachate plumes consists of combinations of two half-reactions: oxidation half-reaction and reduction half-reaction. Table 3 presents the most prominent overall redox reactions, along with their calculated Gibbs free energy change under standard conditions ($\Delta G_0(W)$). The lower (the more negative) the $\Delta G_0(W)$, the more energy is gained,

and the more readily the reaction will proceed. Considering the processes of organic matter oxidation, it is evident that when all electron acceptors are present, oxygen will be used first, followed by nitrate, manganese, iron, and sulfate. Finally, methanogenesis and fermentation reactions dominate, when the most favorable electron acceptors are depleted.

Organic matter dominates the reduction capacity of typical leachates (Christensen *et al.*, 2001). Ammonium and methane may also contribute significantly, showing that the fate of these inorganic compounds in the aquifer may also affect the formation of redox environments. The aquifer OXC may be dominated by iron oxides, when calculated for an aquifer volume including aquifer material and groundwater (Table 4). This is caused by the low aqueous solubility of oxygen, and the relatively low nitrate

Table 3 Most prominent redox reactions in landfill leachate plumes. Dissolved organic matter is represented by the model compound CH_2O.

Reaction	Process	$\Delta G_0 \, (W)$ (kcal mol^{-1})
Methanogenic/fermentative organic matter mineralization	$2CH_2O \rightarrow CH_3COOH \rightarrow CH_4 + CO_2$	-22
Sulfate reduction/OMO	$2CH_2O + SO_4^{2-} + H^+ \rightarrow 2CO_2 + HS^- + 2H_2O$	-25
Iron reduction/OMO	$CH_2O + 4Fe(OH)_3 + 8H^+ \rightarrow CO_2 + 4Fe^{2+} + 11H_2O$	-28
Maganese reduction/OMO	$CH_2O + 2MnO_2 + 4H^+ \rightarrow CO_2 + 2Mn^{2+} + 3H_2O$	-81
Denitrification/OMO	$5CH_2O + 4NO_3^- + 4H^+ \rightarrow CO_2 + 2N_2 + 7H_2O$	-114
Aerobic respiration/OMO	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-120
CO_2 reduction	$HCO_3^- + H^+ + 4H_2 \rightarrow CH_4 + 3H_2O$	-55
Ammonium oxidation	$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$	-72
Methane oxidation	$CH_4 + 2O_2 \rightarrow HCO_3^- + H^+ + H_2O$	-196

Source: Christensen *et al.* (2001).
OMO is short for the reaction organic matter oxidation.

Table 4 Oxidation capacity (OXC, milli equivalent per liter of aquifer) calculated for oxidized species in two aerobic aquifers.

Species	Reduction half-reaction	Vejen (DK)		Sand Ridge (Illinois, USA)	
		Content	OXC (meq L^{-1})	Content	OXC (meq L^{-1})
O_2	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	10 mg L^{-1}	0.44	9 mg L^{-1}	0.39
NO_3^-	$NO_3^- + 6H^+ + 5e^- \rightarrow 1/2N_2 + 3H_2O$	15 mg L^{-1}	1.9	0.95 mg L^{-1}	0.12
Mn(IV) (sediment)	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	0.1 mg g^{-1}	6	0.39 mg g^{-1}	23
Fe(III) (sediment)	$FeOOH + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$	2 mg g^{-1}	60	6.8 mg g^{-1}	200
SO_4^{2-}	$SO_4^{2-} + 9H^+ + 8e^- \rightarrow HS^- + 4H_2O$	40 mg L^{-1}	1.2	36 mg L^{-1}	1.1

The calculations are based on the shown contents of oxidized species, the proposed reduction half reactions, and assumed physical parameters: Porosities of 0.35 and bulk densities of 1.6 kg L^{-1}. The potential contributions from CO_2 and natural organic matter were not evaluated.
Source: Christensen *et al.* (2001).

and sulfate content of aquifers. The actual importance of the dissolved electron acceptors can, however, not be evaluated solely from an aquifer volume. In a flow system the mixing of electron acceptors at the fringes of the plume will be critical as well. Mixing at the fringes will be governed by the transverse dispersivities (transverse and vertical). Seasonal recharge may play a role as well; this was discussed by McGuire *et al.* (2000) for a mixed contaminant plume.

The relative importance of fringe and core processes will also depend on the degradability of the electron donor. In a phenol plume, Thornton *et al.* (2001) showed that the consumption of aqueous oxidants greatly exceeded that of the mineral oxidants. This was in part because very high phenol concentrations limited degradation inside the plume and partly because the iron reduction potential was small in the sandstone aquifer. This is not expected to be the case in a landfill leachate plume in sandy aquifers, as the major electron donor (organic matter) is degradable by iron reduction and there will probably be a large iron reduction capacity. Also, solid

manganese oxides contribute to the OXC, as they can be reduced to dissolved manganese. However, when long-term aquifer changes are in question, iron reduction is likely to dominate, since iron concentrations typically are 20–50 times higher than manganese concentrations in aerobic glaciofluvial sediments (Heron, 1994).

Not all iron oxides are available for reduction. Some iron minerals are solid crystals or even entire iron grains, which makes them resistant to microbial reduction (Lovley, 1991; Postma, 1993; Heron *et al.*, 1994b). Other iron oxides or hydroxides are amorphous and readily reducible. Over time, even some crystalline minerals such as goethite and hematite may be reduced in the complex environment in leachate (Heron and Christensen, 1995). This indicates that the importance of iron as a redox buffer controlling the size of plumes is not given just by the amount of iron oxides present. The composition and microbial availability of iron for reduction are key parameters. Methods for the actual quantification of the microbial iron reduction capacity have, however, not been developed.

Reactive fractions have been addressed by mild chemical extractions (hydrochloric acid or ascorbic acid), but this is only an operationally defined quantity of easily dissolved, oxidized minerals. The actual pool of microbial available iron reduction capacity may be better determined using microbial assays.

The reduction of iron oxides and precipitation of the reduced metals as carbonates or sulfides changes the composition of the solids along a flow line (Figure 3). Overall, the mineral-bound iron oxides are reduced into dissolved ferrous iron, which partly precipitate and partly migrate downgradient into more oxidized zones. When it meets oxygen, and perhaps also manganese oxides, ferrous iron is oxidized and precipitates as amorphous iron hydroxides. The newly precipitated hydroxides form a very reactive and accessible electron acceptor. The migrating part of the reduced iron thus contributes to a regeneration of OXC further away from the landfill. This may be essential in controlling the size of the reduced zones, especially if the plume expands. The substantial buffering by iron oxides, thus, is related to consumption of OXC and the buildup of reduced species in the strongly reduced part of the plume. Overall, iron acts to minimize the size of the plume by the redox buffering reactions, thus greatly retarding the migration of the reduced leachate and associated problematic compounds (Heron, 1994).

9.16.4.2 Microbial Activity and Redox Processes

Inside a landfill leachate plume the environment is characterized by the presence of reduced species and high concentrations of dissolved organic matter. This environment is partly due to the composition of the leachate from the landfill and partly due to microbial processes in the plume. Since this environment is very different from that of uncontaminated, oligotrophic, often aerobic aquifers surrounding the plume, the composition of the microbial population of the plume is dramatically different from the indigenous microbial population of the uncontaminated aquifer.

Microbial populations in landfill leachate-contaminated aquifers are dominated by bacteria (eubacteria and archaea), as shown by analysis of the phospho lipid fatty acids (PLFAs) (Ludvigsen *et al.*, 1999). The total number of bacteria reported in landfill leachate plumes are in the range of $4 \times 10^4 - 1.5 \times 10^9$ cells g^{-1} dry weight (dw) and the number of colony-forming units, living cells, are in the range of $60 - 10^7$ CFU g^{-1} dw (Christensen *et al.*, 2001). However, the large variation caused by different analytical methods and the fact that different types of aquifers were studied mask the difference in the number of bacteria inside and outside the plume. The total number of bacteria in the aquifer downgradient from the Grindsted Landfill (DK) was fairly constant with distance from the landfill, and the ATP content (an estimate of living cells) showed no significant trend (Ludvigsen *et al.*, 1999). In contrast, the number of living bacteria estimated by the PLFA concentration was higher close to the landfill than further away from the landfill. From the measurements of ATP and PLFA, the viable biomass ranged from 10^4 viable cell g^{-1} dw to 10^6 viable cell g^{-1} dw (Ludvigsen *et al.*, 1999), clearly demonstrating the presence of a significantly viable population.

The microbial community structure in the water phase in the landfill leachate plume is clearly different from the community structure outside the plume as shown in the Banisveld aquifer in the Netherlands (Röling *et al.*, 2001) by 16S ribosomal DNA-based denaturing gradient gel electrophoresis (DGGE). Members of the β-subclass of the class *Proteobacteria* dominated upstream of the landfill, but this group was not encountered beneath the landfill where gram-positive bacteria dominated. Further downstream, where the effect of contamination decreased, the community structure shifted partly back; the contribution of the gram-positive bacteria decreased and the β-proteobacteria reappeared. However, the contribution of δ-protoebacteria also increased strongly, and the β-proteobacteria found here (*Acidovorax*, *Rhodoferax*) differed considerably from those found upstream (*Gallionella*, *Azoarcus*) so the community structure continued to be affected by the contamination. Surprisingly, this relationship was not evident in sediment samples, where the major part of the microbial population is present, either because leachate has had little impact on the microorganisms associated with the $10^4 - 10^5$ yr old sediments (Röling *et al.*, 2001), or because the microorganisms in the water phase of the plume were mainly derived from the landfill.

The ability of microbial populations to use different organic substrates under anaerobic conditions was investigated by Röling *et al.* (2000). The contaminated samples were able to use a higher number of substrates than the samples from upstream and downstream. This pattern was observed in water samples as well as in sediment samples, but the populations in sediment samples were able to use up to three times more substrate than populations in water samples (Röling *et al.*, 2000).

Microbial redox processes. Different metabolic types of bacteria (denitrifiers, manganese reducers, iron reducers, sulfate reducers, and methanogens) occur at landfill sites. Some of these metabolic types (sulfate reducers and methanogens) can be separated into physiological

groups which use different carbon substrates as observed in the Norman Landfill (USA) leachate-contaminated aquifer (Beeman and Suflita, 1987, 1990; Harris *et al.*, 1999). The microbial population changed in composition throughout the plume at the Grindsted Landfill (DK). Methanogens and sulfate reducers were abundant close to the landfill, but their numbers decreased in the more distant parts of the plume (Ludvigsen *et al.*, 1999). The iron-, manganese-, and nitrate reducers constituted a surprisingly high fraction of the total cell numbers and their abundance varied little with distance. The ubiquitous presence of these groups of redox specific populations provided the aquifer with a substantial potential for the several redox processes. Therefore, the dominance of one redox process reflects mere the environment and the available electron acceptors than the composition of the microbial population.

The potential for microbially mediated redox processes has been documented in several landfill leachate plumes (Acton and Barker, 1992; Albrechtsen and Christensen, 1994; Nielsen *et al.*, 1995a; Ludvigsen *et al.*, 1998; Cozzarelli *et al.*, 2000). Bioassays of unamended groundwater and sediment samples verified the presence of the following metabolic activities in the Grindsted Landfill (DK) plume: denitrification, iron reduction, manganese reduction, sulfate reduction, and methane production (Ludvigsen *et al.*, 1998). Iron reduction, sulfate reduction, and methane production were also observed at the Norman Landfill (Cozzarelli *et al.*, 2000). Examples of bioassays in different locations within the leachate plume at Grindsted Landfill are shown in Figure 4. The rates for the different processes can be estimated from such incubations, but representative rates cannot be selected. This is due to the fact that only few data exist for landfill sites
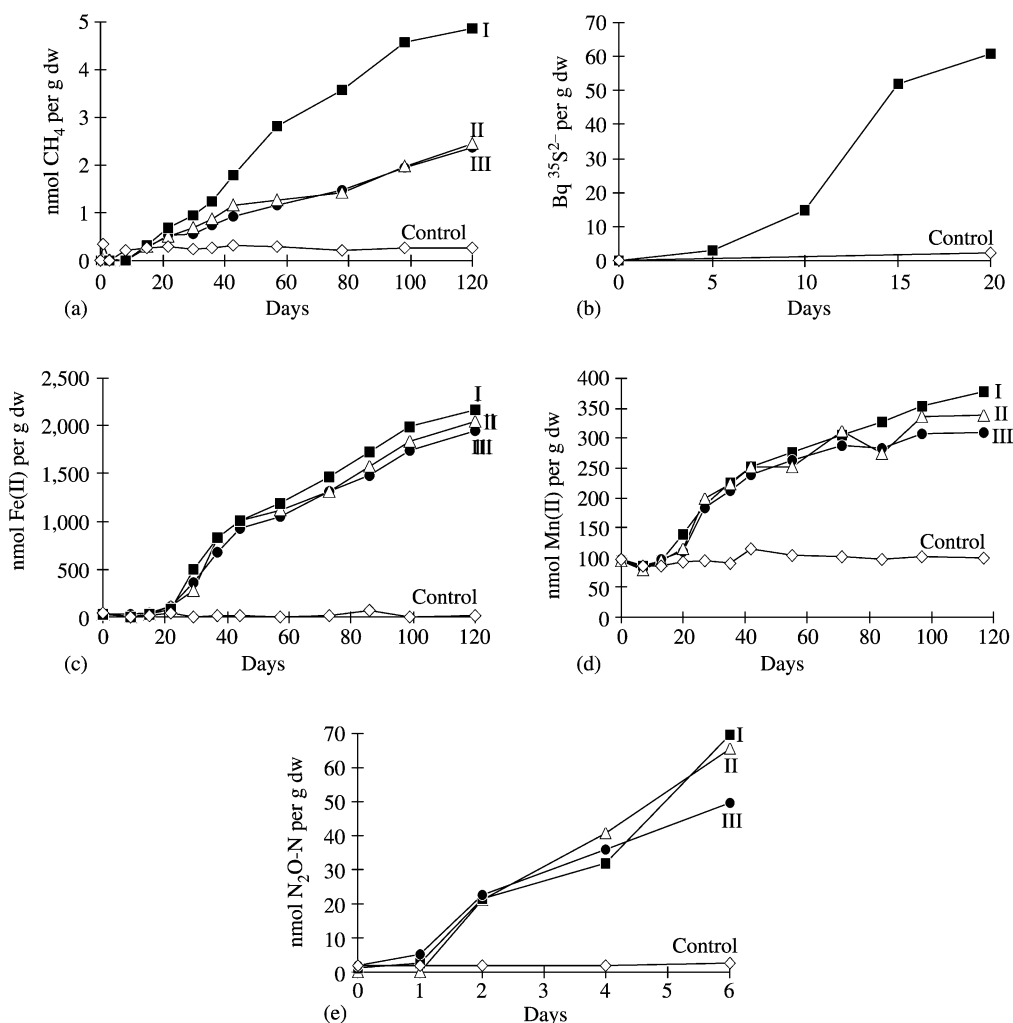
Figure 4 Unamended bioassays showing evidence of each redox reaction from the Grindsted Landfill (DK). The bioassays are performed with sample material from different locations in the plume representing different redox conditions (source Ludvigsen *et al.*, 1998).

(Ludvigsen *et al.*, 1998). That very large variations exist has also been pointed out by McGuire *et al.* (2002), who compared rates in different environments. Several different microbially mediated redox processes occur concomitantly in such microbial assays (Ludvigsen *et al.*, 1998; Cozzarelli *et al.*, 2000), and microbially mediated redox processes do not exclude each other. This somewhat conflicts with a simple thermodynamic model based on Gibbs free energy (Table 3). However, in each sample one electron-accepting process accounted for more than 70% of the equivalent carbon conversion when the measured rates of the electron-accepting processes were used to calculate the carbon conversion of organic matter to carbon dioxide (assuming oxidation level zero of the carbon in the organic matter) (Ludvigsen *et al.*, 1998). This suggests that the concept of redox zones makes sense in terms of dominating redox levels, but that other redox processes may be taking place simultaneously (to be further discussed in Section 9.16.7.2). This may have further implications for the potential of a redox zone to degrade trace amounts of organic chemicals (Rügge *et al.*, 1999a; Albrechtsen *et al.*, 1999).

These microbially mediated redox processes utilize electron acceptors and produce reduced species. This will generate more reduced environments as long as there are electron donors available. The microbial population thus strongly affects their environment in the core of the plume. At the boundaries of the plume, complex microbial communities may exist, and steep redox gradients are created when dissolved electron acceptors are consumed. In addition, reoxidation of sulfides or ferrospecies by oxygen diffusing into the plume may increase the concentration of sulfate and ferric iron, which can stimulate sulfate and iron reduction in these zones as observed at Norman Landfill (Cozzarelli *et al.*, 2000).

In summary, significant numbers of bacteria, detected with several different approaches, are present in landfill leachate plumes. Methanogens, sulfate reducers, iron reducers, manganese reducers, and denitrifiers are believed to be widespread in leachate plumes. Microbial activity seems to occur throughout leachate plumes, although the actual activity (as measured by ATP, PLFA, and redox processes) is low compared to activity in topsoil. Several redox processes can take place in the same samples adding additional diversity to the concept of redox zones illustrated in Figure 3.

9.16.5 OVERVIEW OF PROCESSES CONTROLLING FATE OF LANDFILL LEACHATE COMPOUNDS

The four major compound classes in landfill leachates are dissolved organic carbon, inorganic compound, heavy metals, and XOCs. Typical levels in leachate are reported in Tables 1 and 2. In this section, the fate of these compounds in landfill leachate plumes is summarized. The emphasis is on XOCs, but in order to provide an overview all compound classes are included. A detailed discussion of the fate of individual compounds in landfill leachate plumes can be found in Christensen *et al.* (1994, 2001). A comprehensive investigation of the distribution and geochemistry of inorganic macrocomponents at the Borden Landfill (CAN) is presented by Nicholson *et al.* (1983).

9.16.5.1 Dissolved Organic Matter, Inorganic Macrocomponents, and Heavy Metals

Dissolved organic carbon. Volatile fatty acids constituting a substantial fraction of the dissolved organic carbon in acid-phase leachates are easily degraded according to reported laboratory studies. The dissolved organic matter dominating the methanogenic leachate does not sorb to any substantial degree onto aquifer material and seems fairly recalcitrant with respect to microbial degradation as seen in laboratory experiments (Kjeldsen, 1986). However, with respect to degradation of recalcitrant organic matter, laboratory experiments with short retention times, unstable redox conditions, and limited time for microbial adaptation may fail to simulate the conditions in a leachate polluted aquifer. Observations of actual leachate plumes are usually too limited to provide insight into the fate of the dissolved organic matter. One exception is the report by Lyngkilde and Christensen (1992a) that demonstrated substantial degradation of dissolved organic matter in the anaerobic part of the leachate plume at Vejen Landfill (DK). The observations by DeWalle and Chian (1981) and Rügge *et al.* (1995) may support this, indicating that dissolved organic matter in methanogenic leachate is degradable to a large extent. Brun *et al.* (2002) quantified the degradation of organic carbon in the Vejen Landfill leachate plume. They found half-lives of 100 d in the anaerobic parts of the plume and $1-2$ d in the aerobic zone. The anaerobic degradation rate is comparable to that of Sykes *et al.* (1982), who estimated an anaerobic half-life at the Borden Landfill (CAN) of 400 d.

Inorganic macrocomponents. Anions in leachate plumes are mainly important due to their ability to form complexes, take part in dissolution/precipitation processes, and their role as electron acceptors. The formation of complexes may increase the mobility of cations and heavy metals. In addition, many reactions are influenced by pH, which is governed, to a large extent, by the carbonic acid components, in particular HCO_3^-.

The sulfur compounds involved in the sulfate-reduction process are of interest, but the prevalence of sulfate reduction in leachate plumes is not very well understood (Murray *et al.*, 1981). Nitrate and perhaps sulfate as well may be depleted in the core of the plume, but they are certainly significant players at plume boundaries.

The attenuation of cations is primarily governed by cation-exchange processes in addition to dilution (Nicholson *et al.*, 1983). Calcium and magnesium are also influenced by complexation and dissolution/precipitation processes. The attenuation of ammonium and potassium due to cation-exchange processes is significant, while sodium takes little part in cation-exchange processes. Calcium and in some cases also magnesium, typically dominate the cation-exchange complex, can be released and moved to the front of the leachate plume (Kehew *et al.*, 1984).

Ammonium seems to be significantly attenuated in the anaerobic part of the plume as indicated by the detailed investigation of the Grindsted Landfill (DK) leachate plume. The ammonium plume is of limited extent. It is followed by zones of increasing concentration of nitrate and dinitrogen oxide, but the attenuation mechanisms of ammonium are not understood. This issue deserves further research, as ammonium may be seen as one of the critical compounds in landfill leachate plumes (Christensen *et al.*, 2000a).

Dissolved iron and manganese in the leachate are subject to precipitation as sulfides or carbonates, ion exchange, oxidation, and dilution (Nicholson *et al.*, 1983). These processes tend to lower the aqueous concentration of iron and manganese along the flow lines, but reduction of sediment-associated iron and manganese oxides may increase their concentrations further out in the plume (Albrechtsen and Christensen, 1994). Sometimes they are often supersaturated with respect to carbonates (Jensen *et al.*, 2002). Organic complexation of iron and manganese seems only of modest importance. Further down-gradients in the landfill redox potentials are higher, so that iron and manganese may reprecipitate as oxides.

Heavy metals. The behavior of heavy metals in a landfill leachate plume is simultaneously controlled by sorption, precipitation, and complexation, and proper evaluations of metal attenuation must account for this complex system. Generally, heavy metals do not constitute a groundwater pollution problem at landfills (Arneth *et al.*, 1989), because landfill leachates usually contain only modest heavy metal concentrations, and the metals are subject to strong attenuation by sorption and precipitation in the landfill itself (Kjeldsen *et al.*, 2002). Sulfide-producing conditions result in extremely low solubility of the heavy metals (Bisdom *et al.*, 1983). The presence of colloidal as well as organically complexed metals enhances solubilities and mobilities (Christensen *et al.*, 1996), but apparently not to the extent that the metals migrate appreciably in leachate plumes.

9.16.5.2 Xenobiotic Organic Compounds

Sorption. In aquifers characterized by low organic carbon content, most of the XOCs found in leachate plumes are only weakly attenuated by sorption. This applies to the aromatic hydrocarbons, chlorinated hydrocarbons, and the polar compounds. Very few detailed sorption studies involving landfill leachate have been reported (Kjeldsen *et al.*, 1990; Larsen *et al.*, 1992). Preliminary evidence suggests that the presence of leachate, in particular in terms of dissolved organic carbon, does not affect the sorption of XOCs significantly and as such the traditional methods for estimating retardation in aquifers are valid.

The chlorinated aliphatic hydrocarbons are frequently identified in landfill leachate. Adriaens *et al.* (see Chapter 9.14) reviewed their presence and fate in the environment. The chlorinated aliphatic hydrocarbons generally degrade by reductive dechlorination under anaerobic conditions (Vogel *et al.*, 1987). The understanding of this process has increased during the last few years, and it is now generally accepted that the chlorinated compounds can act as electron acceptors (halorespiration; Holliger *et al.* (1999)). This also means that the reductive dechlorination process requires an electron donor such as naturally occurring carbon, petroleum hydrocarbons, or organic carbon in landfill leachate. The greater availability of naturally occurring carbon likely contributes to the extremely rapid reductive dechlorination of chlorinated ethanes and ethenes that was observed in wetland sediments compared to sand aquifers (Lorah and Olsen, 1999a,b; Lorah *et al.*, in press). Degradation of higher chlorinated aliphatic compounds such as tetrachloroethylene (PCE) and trichloroethylene (TCE) under aerobic condition has not been demonstrated, but degradation products such as dichloroethylene (DCE) isomers (primarily *cis*-1,2-DCE) can be oxidized to carbon dioxide. Recent microcosm studies with aquifer and streambed sediments indicate that oxidation of *cis*-DCE and vinyl chloride (VC) to carbon dioxide may also be possible under manganese and iron-reducing conditions (see a review by Bradley (2000)), although the occurrence and significance of this reaction in contaminant plumes has not been demonstrated. In microcosm and enrichment experiments with

wetland sediments, Jones *et al.* (2002) found that addition of Fe(III) either as amorphous FeOOH or as Fe(III)NTA slowed dechlorination of chlorinated ethanes and inhibited degradation of *cis*-DCE, *trans*-DCE, and VC. Degradation of the chlorinated ethanes and ethenes was most rapid under methanogenic conditions (Jones *et al.*, 2002; Lorah *et al.*, in press).

Information obtained from different plumes is in accordance with observations from landfill leachate plumes, where the expectation is that PCE and TCE will be reductively dechlorinated. This is supported by observations of lower chlorinated compounds, DCE and VC, in leachate plumes or degradation experiments. The transformation of chlorinated ethenes has been observed under various redox conditions ranging from methanogenic to nitrate-reducing conditions (Nielsen *et al.*, 1995a; Johnston *et al.*, 1996; Bradley, 2000; Rügge *et al.*, 1999a). Tetrachloromethane will rapidly degrade in landfill plumes by reduction with sediment-associated iron and organic carbon (Rügge *et al.*, 1999a; Pecher *et al.*, 1997). The transformation of 1,1,1-TCA in anaerobic environments is rapid and seems to be affected by both abiotic and biotic degradation processes (Bjerg *et al.*, 1999; Nielsen *et al.*, 1995b). Studies of full-scale landfill plumes have shown a significant degradation of TCE (Chapelle and Bradley, 1998) and 1,1-DCA (Ravi *et al.*, 1998). However, in the case of 1,1-DCA, complete dechlorination to ethane was not shown. In summary, the information available suggests that landfill plumes host redox environments, microorganisms, and/or geochemical processes that can effectively attenuate chlorinated aliphatic hydrocarbons.

The aromatic hydrocarbons generally degrade readily under aerobic conditions, but anaerobic degradation by pure bacterial cultures has also been recognized (see Chapter 9.12; Heider *et al.*, 1999). The vast amount of data from natural attenuation studies of petroleum hydrocarbon plumes generally supports anaerobic degradation, especially for benzene, toluene, ethylbenzene, xylenes (BTEX) under field conditions. The first-order degradation rates observed under unspecified anaerobic conditions (Suarez and Rifai, 1999) are typically one or two orders of magnitude lower than rates reported under aerobic conditions (Nielsen *et al.*, 1996).

Detailed observations in landfill leachate plumes have indicated the degradation mainly of toluene, xylenes, and C3–C5 benzenes (Barker *et al.*, 1986; Lyngkilde and Christensen, 1992b; Rügge *et al.*, 1995; Eganhouse *et al.*, 2001). These studies use tracers or compound ratios to rule out dilution and sorption; however, direct proof of degradation has not been provided. Isotopic ratios have been introduced as a powerful tool for identification of degradation. The Vejen Landfill (DK) site was revisited after 10 yr (Baun *et al.*, 2003; Richnow *et al.*, 2003) and evidence of degradation was provided for ethylbenzene and *m/p*-xylene by using the isotopic ratio $^{13}C/^{12}C$ in aromatic hydrocarbons. A specific degradation product, benzyl succinic acid (see a review by Beller (2000)), was observed. This documents the degradation of toluene in the plume. Positive results regarding the degradation of benzene are few. Baun *et al.* (2003) concluded that benzene was persistent in the anaerobic part of the Vejen Landfill (DK) plume. Ravi *et al.* (1998) proved that benzene degradation took place in the very long plume at West KL Landfill (USA).

The degradability of toluene and xylenes observed in plumes has been supported by experimental evidence from field and laboratory experiments (Acton and Barker, 1992; Bjerg *et al.*, 1999; Nielsen *et al.*, 1995a; Johnston *et al.*, 1996; Rügge *et al.*, 1999a), while the recalcitrance of benzene has been shown in experiments by the same authors. This adds to the belief that benzene is less readily degradable than most of the other BTEXs under strongly anaerobic conditions in landfill leachate plumes.

The phenolic compounds generally degrade readily under aerobic conditions. Information for anaerobic conditions is mixed, and no distinct pattern has emerged. Studies indicate persistence of phenol, *o*-cresol, 2,4-dichlorophenol, and 2,6-dichlorophenol under iron-reducing and nitrate-reducing conditions (Nielsen *et al.*, 1995a). Grbic-Galic (1990) reviewed the methanogenic transformation of phenolic and aromatic compounds in aquifers in more general terms, and reported the transformation of several phenols.

The pesticides are another important group of pollutants (see Chapter 9.15). Many different herbicides have been identified in landfill leachate; however, very little is known about pesticide degradation potentials in leachate plumes. Mecoprop is frequently observed in leachates (Table 2). At the Vejen Landfill (DK), mecoprop was observed in the plume 130 m downgradient of the landfill at a concentration of 95 μg L^{-1} (Lyngkilde and Christensen, 1992b). Baun *et al.* (2003) showed in a revisit to the site that MCPP was recalcitrant in the anaerobic part of the plume up to 135 m from the landfill. In an injection experiment in the Grindsted Landfill (DK) plume Rügge *et al.* (1999b) found that atrazine and mecoprop were recalcitrant under strongly anaerobic conditions. Anaerobic dechlorination of phenoxy acids has been proposed. Rügge *et al.* (1995) identified phenoxy acids resembling known herbicides, though, without the chlorine atoms attached in landfill leachate-affected groundwater. Tuxen *et al.* (in press) proposed that a significant part of the phenoxy

acids at the Sjoelund Landfill (DK) disappeared due to degradation in the interphase between the anaerobic leachate plume and the surrounding aerobic aquifer. This is consistent with the expected aerobic degradation of phenoxy acids (Broholm *et al.*, 2001). In conclusion, studies on pesticide degradation in different anaerobic environments are few, and due to their general recalcitrance in groundwater environments (Albrechtsen *et al.*, 2001), pesticides may turn out to be critical compounds in landfill leachate plumes.

Recently, information on XOC degradation in different landfill plume redox environments has been expanded. As more results become available, more XOCs are found to be degradable in the intermediate redox zones dominated by sulfate, iron, and nitrate reduction. Transformation of chlorinated aliphatics seems to occur not only under methanogenic conditions, but also in less reducing zones. Aromatic hydrocarbons degrade readily in aerobic environments, but only slowly in reducing environments. Benzene may, in particular, be recalcitrant under strongly reducing conditions. As our ability to perform degradation studies has improved significantly since the 1990s, more detailed information on complex degradation patterns and compound interactions has been revealed. Also, the use of isotopic ratios and the identification of specific degradation products has improved our ability to demonstrate degradation under field conditions. Several compounds have been shown to disappear in plumes, but direct evidence of microbial degradation has only been established for some of these XOCs. Finally, the frequent occurrence of pesticides and the presence of more polar compounds also call for a greater focus on these compounds.

9.16.6   NORMAN LANDFILL (USA)

The Norman Landfill Research Site is a closed municipal solid waste landfill, formerly operated by the city of Norman, Oklahoma. The site is a research site of the Toxic Substances Hydrology Program of the US Geological Survey (USGS). Scientists from the USGS, the University of Oklahoma, the US EPA, and numerous universities have installed wells and instruments to investigate the chemical, biological, and hydrologic processes in groundwater and surface water affected by landfill leachate. At Norman Landfill, a combined geochemical and microbiological approach has been used to identify the important biogeochemical processes occurring in the aquifer contaminated by leachate from the Norman Landfill (Cozzarelli *et al.*, 2000; Harris *et al.*, 1999).

9.16.6.1   Source, Geology and Hydrogeology

The field site is located in the alluvium of the Canadian River. The landfill has received solid waste since 1922. The waste was dumped into trenches that were ~3 m deep and that contained water to a depth of 1.5–2.5 m because of the shallow water table; the waste was subsequently covered with 15 cm of sand. No restrictions were placed on the type of material dumped at the landfill. In 1985 the landfill was closed, and the mounds, which had reached a maximum height greater than 12 m, were covered with local clay and silty-sand material. The Canadian River alluvium is 10–12 m thick and consists predominantly of sand and silty sand, with interbedded mud and gravel. Near the landfill the water table is less than 2 m below the land surface. The hydraulic conductivity of subsurface materials near the landfill, which was measured using slug tests, ranged from 7.3×10^{-2} m d^{-1} to 24 m d^{-1} (Scholl *et al.*, 1999). A discontinuous, low hydraulic-conductivity interval that consisted of silt and clay was detected ~3–4 m below the water table along the transect (A–A$'$) where most data have been collected (Figure 5). A high hydraulic-conductivity layer containing coarse sand and gravel is located near the base of the alluvium at depth of ~10–12 m. Low-permeability shales and siltstones of the Hennessey Group of Permian age underlie the alluvium, and act as a boundary to vertical groundwater flow. A shallow stream with areas ponded by beaver dams (referred to here as sloughs), which is ~0.75 m deep, lies roughly parallel to the landfill and ~100 m to the southwest (Figure 5). Groundwater flows from the landfill toward the slough and Canadian River.

9.16.6.2   Landfill Leachate Plume

Biogeochemistry of plume. Chloride and non-volatile dissolved organic carbon (NVOC) profiles along the well 35–80 transect confirm that the plume extends through the entire thickness of the alluvium between the landfill and the slough and has migrated beneath the slough (Figures 6(a) and (b)). Groundwater downgradient from the landfill has high concentrations of NVOC compared to groundwater collected upgradient and northeast of the landfill, where the average concentration is <0.2 mM (Cozzarelli *et al.*, 2000). The high NVOC concentrations result from the dissolution and partial degradation of organic waste in the landfill. The maximum concentration of NVOC (17 mM) was measured close to the landfill edge.

Degradation of organic compounds to inorganic carbon compounds is shown by the increase in
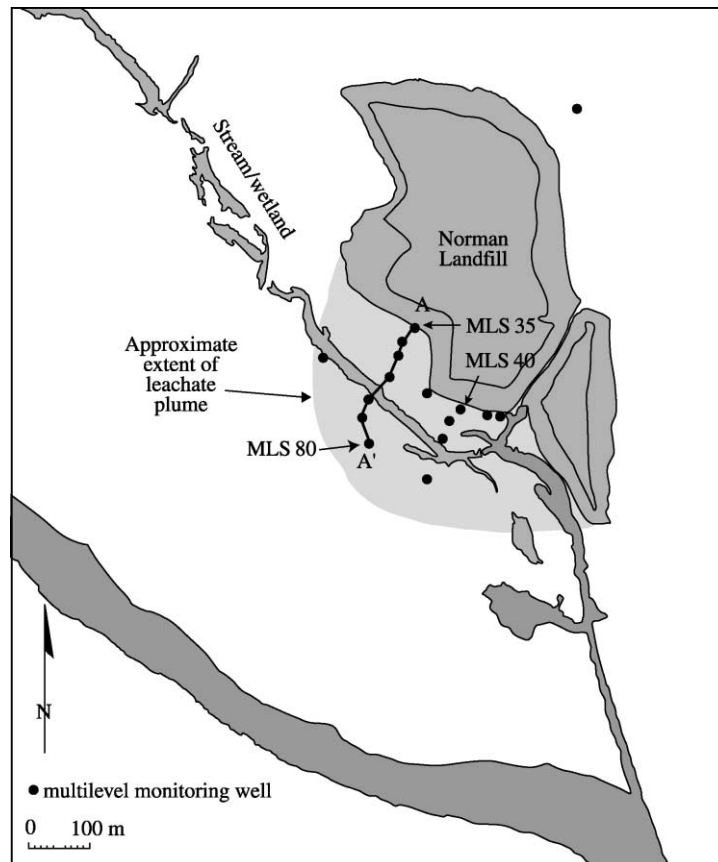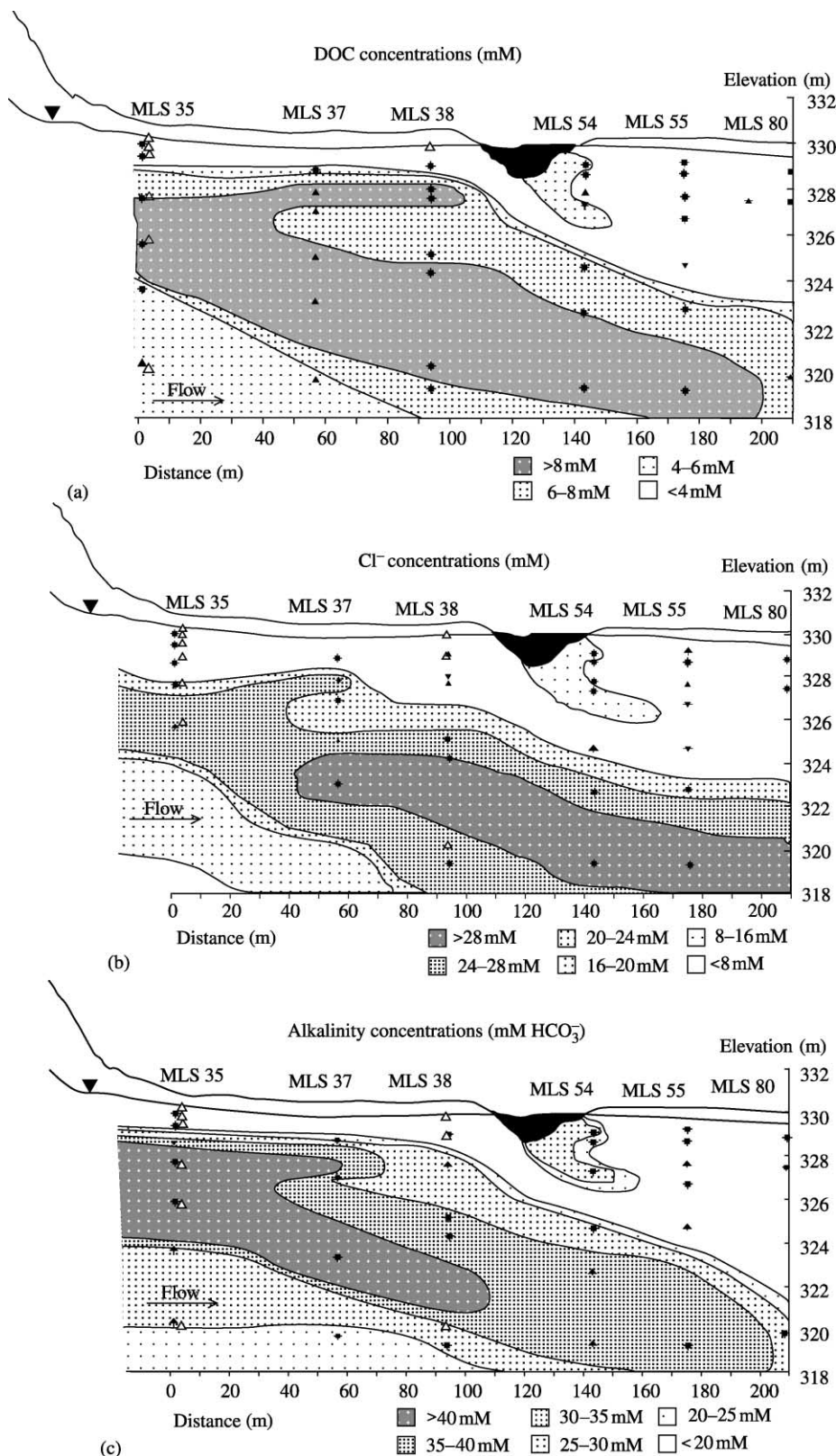
Figure 5 Map showing the Norman Landfill (USA) site. Transect A–A′ runs from MLS 35 to MLS 80 in the direction of groundwater flow. The approximate extent of the plume was determined from geophysical measurements and specific conductance measurements.

alkalinity (up to 7 times the background concentration) of groundwater downgradient from the landfill resulting in an alkalinity plume similar in shape to the NVOC plume (Figure 6(c)). Background water pH values ranged from 6.9 to 7.3, whereas values throughout the high chloride plume along transect A–A′ (Figure 5) ranged from 6.7 to 7.3. Degradation processes in the leachate-contaminated aquifer have resulted in the depletion of oxidized chemical species (such as O_2 and SO_4^{2-}) and the accumulation of reduced products (such as Fe^{2+}) in the groundwater (Figure 6(d)). The entire area that was sampled between the landfill and the slough is anaerobic (<5 μM dissolved oxygen). Aerobic respiration is of limited importance in most of the contaminated aquifer. High levels of ammonium are present in the groundwater immediately downgradient from the landfill (>5 mM, Figure 6(e)) and nitrate levels in the contaminated aquifer and in the background water are very low (<0.1 mM). The large NH_4^+ plume downgradient from the landfill is probably due to the transport of NH_4^+ produced during the fermentation of organic matter within the refuse mounds. At the boundary of the plume

the concentration of NH_4^+ decreases sharply. Ammonium bound by cation exchange onto sediment or oxidation along the plume boundary may control the transport of ammonium. Periodically, nitrate concentrations as high as 2.7 mM were measured in 1999 during monthly sampling of water table wells. NH_4^+ oxidation probably occurs in this zone.

High concentrations of Fe^{2+} in the groundwater (>0.25 mM, Figure 6(d)) are consistent with microbial dissolution of iron oxides in the aquifer. Reactive iron oxides were depleted from sediments within the contaminated region of the aquifer (Harris *et al.*, 1999). Hematite grain coatings remained on all samples collected within the anaerobic plume (Breit *et al.*, 1996) and may be available as a source of electron acceptors for iron-reducing bacteria. Nevertheless, the persistence of hematite relative to iron oxyhydroxides in the Norman Landfill plume suggests that the microbial reduction of hematite, if it occurs at all, is very slow.

Sulfate reduction in the plume has resulted in the depletion of SO_4^{2-} from the center of the plume (Figure 6(f)). Dissolved sulfate at the

DOC concentrations (mM)

(a)

>8 mM   4–6 mM
6–8 mM   <4 mM

Cl⁻ concentrations (mM)

(b)

>28 mM   20–24 mM   8–16 mM
24–28 mM   16–20 mM   <8 mM

Alkalinity concentrations (mM HCO₃⁻)

(c)

>40 mM   30–35 mM   20–25 mM
35–40 mM   25–30 mM   <20 mM

Figure 6 Distribution of: (a) NVOC concentrations (in mM); (b) chloride (Cl⁻) concentrations (in mM); (c) alkalinity values (in mM HCO₃⁻); (d) ferrous iron concentrations (in mM); (e) ammonium concentrations (in mM); (f) sulfate concentrations (in mM) and methane concentrations (in mM, shown in the plot as individual values at sites 35 and 38), in groundwater downgradient from the Norman Landfill along a transect from site 35 to 80 (after Cozzarelli *et al.*, 2000).
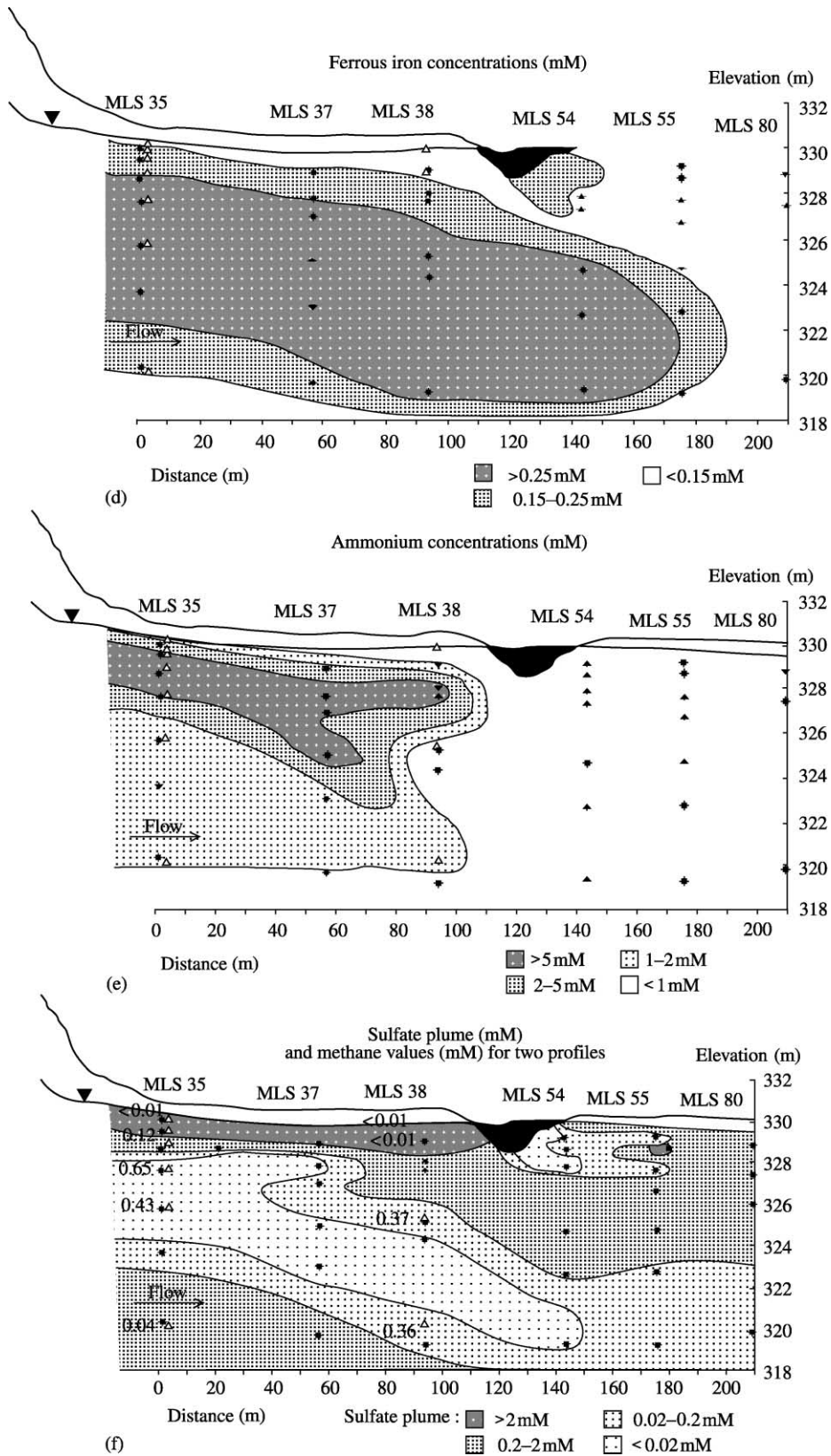
Figure 6 (continued).

edge of the landfill (site 35) was enriched in ^{34}S. At the water table (1.0 m below land surface (bls)), the $\delta^{34}S$ of SO_4^{2-} was 33‰; 1.6 m bls, the $\delta^{34}S$ of SO_4^{2-} was 67‰. In contrast, sulfur-isotope analyses of SO_4^{2-} in groundwater from uncontaminated alluvium showed that the $\delta^{34}S$ of SO_4^{2-} was −5‰ at 1.0 m bls. Although dissolved sulfide concentrations in the plume were low (0.3–5.0 μM), analysis of the sediment cores indicated that iron sulfides have accumulated in the aquifer. The highest concentrations of iron sulfides were detected just beneath the water table where increased sulfate reduction rates were measured (Figure 7).

Concentrations of CH_4 are highest in the center of the anoxic plume. The highest CH_4 concentrations occurred slightly beneath the top of the sulfate-depleted zone (Figure 6(f)). The δD values for groundwater downgradient from the landfill indicate that the groundwater is enriched in deuterium (Cozzarelli *et al.*, 2000). Hackley *et al.* (1996) reported 30–60‰ deuterium enrichment in leachate from three landfills in Illinois, and speculated that most of the enrichment was a result of methanogenesis, with some enrichment resulting from isotopic exchange with hydrogen sulfide. The greatest enrichment in deuterium at the Norman Landfill was measured in the center of the plume where δD of H_2O values ranged from −10.6‰ to −3.4‰, compared to background values of −45.8‰ to −27.9‰. The samples that contained the greatest enrichment in deuterium also had total inorganic carbon (TIC) values enriched in ^{13}C. The $\delta^{13}C$ of TIC in the most contaminated groundwater downgradient from the landfill was as heavy as 11.9‰. This indicated a significant enrichment in ^{13}C compared to typical

$\delta^{13}C$ values of shallow groundwater from the Central Oklahoma aquifer, which ranged from −17.8‰ to −12.5‰ (Parkhurst *et al.*, 1993). This large shift in isotopic composition to enriched values in the groundwater most likely results from biogenic CH_4 production. The high concentrations of CH_4 combined with the heavy δD of H_2O values at the edge of the landfill at Norman, Oklahoma indicate that methanogenesis probably occurs within and underneath the landfill, and that the products of this process are transported in groundwater.

Availability of electron acceptors. The fate of NVOC was investigated in the plume (Figure 6). The NVOC concentrations show little change with distance, indicating that NVOC is not efficiently degraded in this zone. Most of the degradation occurs at the boundaries of the plume where electron acceptors are available (Figure 7). Direct rate measurements made in the laboratory combined with field observations suggest that sulfate reduction and methanogenesis are the most important microbial reactions that affect aquifer geochemistry downgradient from the Norman Landfill. Although the core of the plume is strictly anaerobic and supports both sulfate reduction and methanogenesis, the edges of the plume appear to support iron reduction and, to a greater extent, sulfate reduction, due to the increased availability of readily reactive electron acceptors at these boundaries. The nonuniform availability of electron acceptors and the mixing of the contaminant plume with oxygenated water at the plume boundaries have a significant effect on biogeochemical processes.

Soluble and solid-phase geochemical investigations coupled with laboratory rate experiments
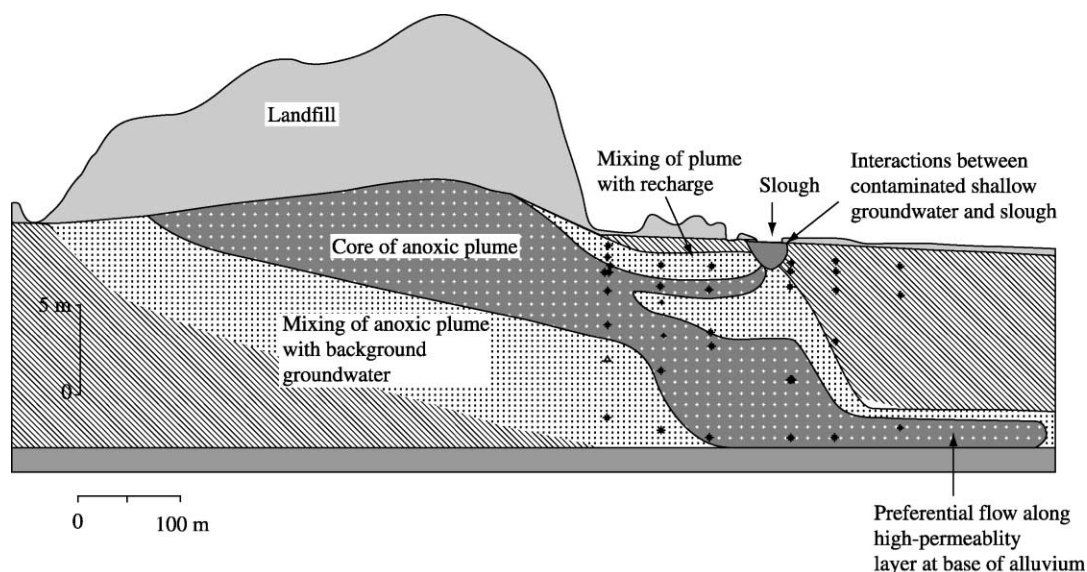
Figure 7 Conceptual model of redox (transport and reaction) zones at the Norman Landfill (USA).

were used to evaluate the factors that control the availability of electron acceptors in this system (Cozzarelli *et al.*, 2000; Ulrich *et al.*, 2003). The sources of electron acceptors vary significantly over relatively small spatial scales (on the order of meters). At least three sources of sulfate that support sulfate-reducing activity in the leachate-impacted aquifer have been identified. Each of these sources supplies sulfate to a different region of the aquifer.

First, the oxidation of iron sulfides to sulfate and/or dissolution of sulfate during recharge events are important in shallow regions near the water table where high rates of sulfate reduction have been measured. *In situ* evidence for aerobic iron sulfide oxidation is found at the water table, where despite relatively high rates of sulfate reduction, the concentration of iron sulfide is comparatively low (Figure 8). Further, sulfate concentrations are highest near the water table and decrease rapidly with depth. Experiments conducted with sediment collected from the study site have shown that hydrogen sulfide leaves the solution rapidly as a constituent of immobile iron sulfide minerals in the sediments. Such minerals were not easily oxidized to sulfate under anaerobic conditions in the presence of a variety of potential electron acceptors (Ulrich *et al.*, 2003). However, when aerobic conditions prevail, as is expected to occur seasonally at the water table, the iron sulfides readily oxidize and the sulfate concentration increases. The observation that iron sulfide oxidation near the water table contributes to the supply of SO_4^{2-} is

analogous to findings from an uncontaminated aquifer in the Yegua formation of East Central Texas (Ulrich *et al.*, 1998).

Sulfate reduction within the core of the plume (at intermediate aquifer depths) is limited by the availability of sulfate, which is supplied by the slow process of barite ($BaSO_4$) dissolution. Under conditions of low dissolved sulfate ($<10\ \mu M$), as is the case in the center of the anaerobic leachate plume, barite is undersaturated and dissolves, releasing both barium and sulfate to solution. Barite grains within the core of the plume show dissolution features (Figure 9). Rapid dissolution of barite is unlikely given its low solubility; however, the amount of barite present in the sediment is sufficient to impact the sulfate budget of the aquifer (Ulrich *et al.*, 2003).

Another source of sulfate in the aquifer is advection just above the confining layer at the bottom of the aquifer. Hydraulic conductivity is relatively high (Scholl and Christenson, 1998) in this depth interval, where coarse-grained sands and gravel are the dominant sediment types. The lower chloride concentration and the lower specific conductance of groundwater in deeper portions of the aquifer relative to the leachate plume are consistent with mixing of leachate with uncontaminated groundwater. Dissolved sulfate in this interval approaches background concentrations and is important in maintaining rates of sulfate reduction. Investigations of plume biogeochemistry (Cozzarelli *et al.*, 2000) indicate that the influx of electron acceptors by mixing with
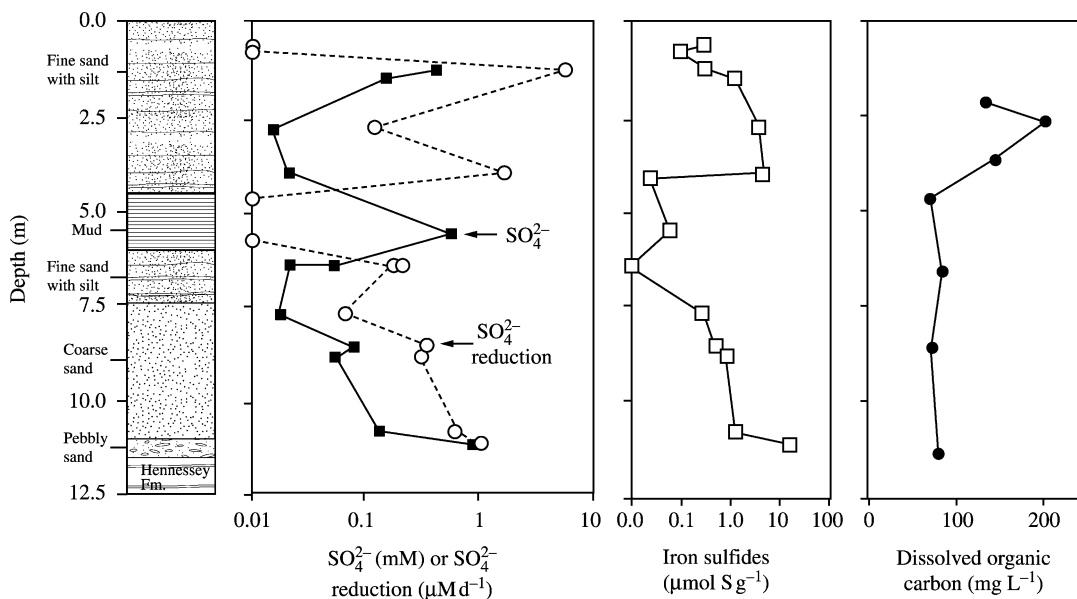
Figure 8 Depth profile (meters below land surface) of the stratigraphy, sulfate reduction rates, sulfate concentration, iron sulfide content of sediments, and dissolved organic carbon in groundwater obtained from an area adjacent to well 40 (source Ulrich *et al.*, 2003).
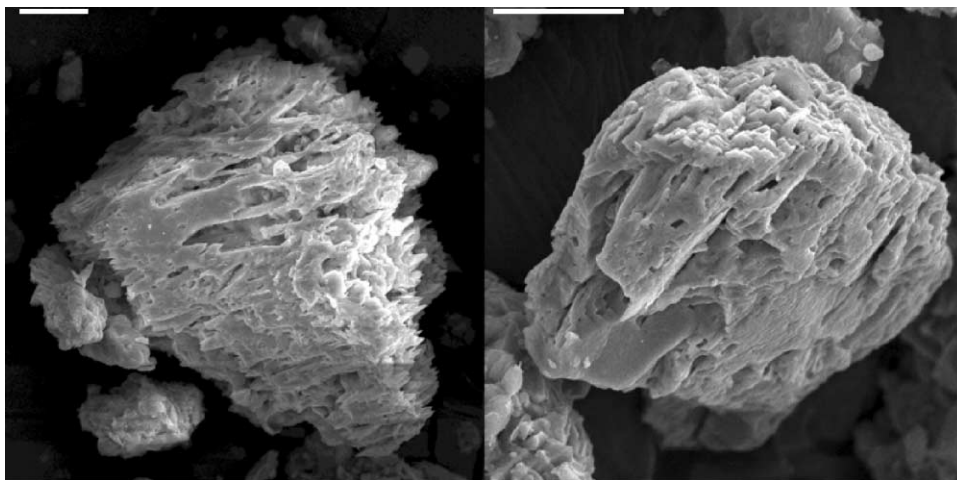
Figure 9 SEM micrographs contrasting textures of detrital barite grains. Grain on the left with dissolution textures was collected from sediment exposed to leachate; nearby pore water contains <10 mg L^{-1} sulfate. Grain on the right was collected from sediment unexposed to leachate and containing 100 mg L^{-1} sulfate. Bar scale is 10 μm (source Ulrich *et al.*, 2003).

recharge or upgradient groundwater is limited to the boundaries of the plume.

Fate of XOCs. Investigation of the distribution of VOCs has provided evidence of natural attenuation of several priority pollutants (Eganhouse *et al.*, 2001). Although VOCs make up <1% of the mass of organic carbon in the Norman Landfill leachate plume, they are useful indicators of biodegradation in the leachate plume. Eganhouse *et al.* (2001) compared the concentrations of two isomers of benzene, isopropylbenzene, and *n*-propylbenzene, in landfill leachate. Isomers of benzene have the same number and type of atoms, but the molecules have slightly different structures. These isomers of benzene have similar physical properties; they should, therefore, be affected similarly by volatilization, dilution, and sorption. Thus, comparisons of the concentration of this pair of compounds, which changes with the distance from the source, allow for the elaboration of the processes responsible for the observed attenuation. The basis for this analysis is that compounds having identical or very similar physico-chemical properties should have the same distribution within a given region of the plume unless differences in compound-specific biodegradation rates cause them to differ (Reinhard *et al.*, 1984; Eganhouse *et al.*, 1996, 2001; Allen-King *et al.*, 1996). The concentration of *n*-propylbenzene decreases much faster as leachate flows away from the landfill than the concentration of isopropylbenzene. This rapid decrease in the concentration of *n*-propylbenzene at Norman Landfill is caused by biodegradation. These techniques can be applied at sites with contaminants other than landfill leachate.

In situ field experiments of microbial processes in zones with different chemical and physical properties have been conducted at Norman Landfill using push–pull test technology and small-scale tracer tests (Scholl *et al.*, 2001; Senko *et al.*, 2002). Push–pull tests are single-well injection-withdrawal tests (Istok *et al.*, 1997). During the injection phase of the test, a solution consisting of groundwater spiked with tracers, electron donors, or electron acceptors is injected or "pushed" into the aquifer. During the extraction phase, the test solution is pumped ("pulled") from the same location and the concentrations of tracers, reactants, and possible reaction products are measured as a function of time in order to construct breakthrough curves and to compute mass balances for each solute. Reaction rate coefficients are computed from the mass of reactant consumed and/or product formed. These tests can be conducted anywhere in an aquifer, making it possible to investigate processes and rates in different geologic and geochemical environments.

At Norman Landfill investigators are using these field injection techniques to investigate how biodegradation rates vary with aquifer permeability (Scholl *et al.*, 2001). Push–pull tracer tests were conducted to measure *in situ* biodegradation rates of simple organic acids in the leachate plume. Replicate wells were placed in three layers: medium sand, silt/clay lenses in sand, and poorly sorted gravel. The *in situ* biodegradation rates of two simple organic acids, formate and lactate, were compared in three different permeability zones within the anoxic leachate plume at the site. These organic acids were used, because they degrade

at different rates depending on the dominant microbial processes. The results show that there are differences in biodegradation rates in areas of different permeability. These may be related to differences in microbial community structure, sediment chemistry, and water flow regime.

The conceptual model of biogeochemical zones developed for the Norman Landfill study (Figure 7) provides a framework for understanding the transport of organic contaminants and provides insight into the natural attenuation of the concentration of leachate compounds in the aquifer. This type of approach to assessing the active microbial processes and the availability of electron acceptors can be applied at other sites contaminated with leachate. Once the biogeochemical framework of a system is established, detailed experiments on the rates of processes and the fate and transport of the compounds of concern can be undertaken.
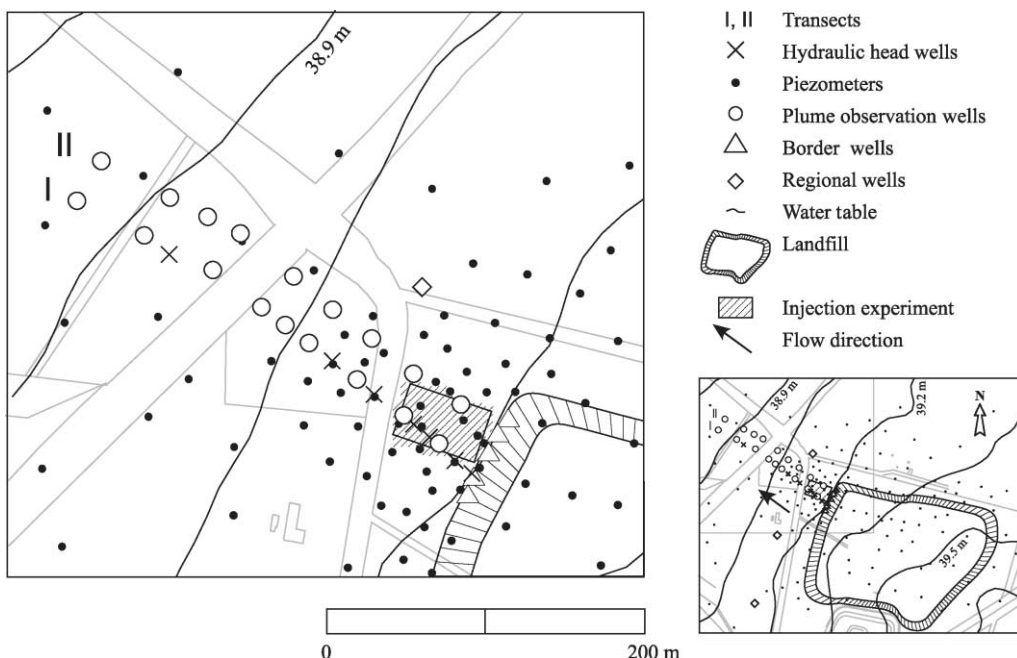
9.16.7 GRINDSTED LANDFILL SITE (DK)

The Grindsted Landfill site in Denmark has been subjected to a number of investigations since 1992. The site has been investigated using a multidisciplinary approach by a large group of researchers of different background (environmental engineering, environmental chemistry, ecotoxicology, geology, and microbiology) from the Technical University of Denmark. The work has been done in co-operation with researchers from universities and research institutions all over the world.

9.16.7.1 Source, Geology and Hydrogeology

The site is located in the western part of Denmark on top of the original land surface (Figure 10). Disposal of waste took place between 1930 and 1977. Approximately, 3×10^5 t of waste were deposited there, mainly between 1960 and 1970 (Kjeldsen *et al.*, 1998a). The waste consists of: municipal solid waste (20%); bulky waste, garden waste, and street sweepings (5%); industrial waste (20%); sewage treatment sludge (30%); and demolition waste (25%). The spatial variability of the leachate quality was investigated by sampling (31 wells) below the landfill in the uppermost groundwater (a small unsaturated zone exists beneath the landfill). The results revealed a significant spatial variability in the leachate composition. Based on these results, landfill could be divided into four main areas (Figure 11). The average concentrations of ammonium, chloride, and NVOC in the strong leachate were typically 20–40 times higher than in the weak leachate. The strong leachate was located in the northern part of the landfill and originated from the dumping of industrial waste. The large heterogeneities in leachate quality may generate plumes with different properties and call for different remedial actions mainly directed towards the industrial hot spot area.

Geology. The Grindsted Landfill is located on a glacial outwash plain. The upper 10–12 m of the unconfined aquifer consist of an upper Quaternary sandy layer and a lower Tertiary sandy layer, locally separated by discontinuous silt and clay layers (Heron *et al.*, 1998). Investigations of the


Figure 10 Location of the Grindsted Landfill (DK) site, overview of wells, and investigated transects.
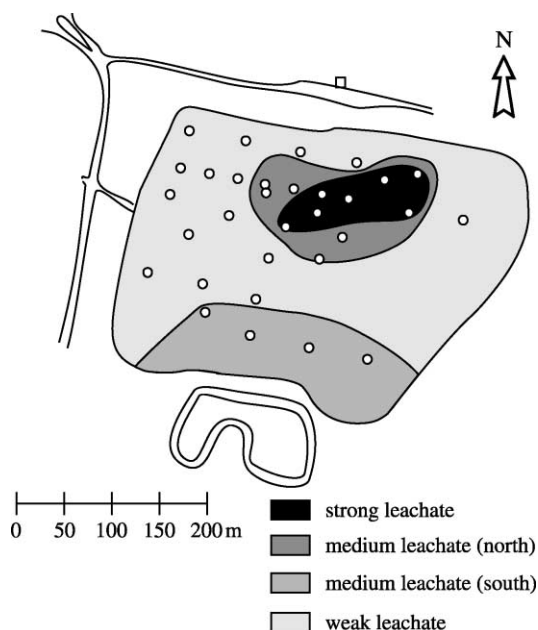
Figure 11 Division of the landfill into four areas with different leachate strength. The division was primarily based on chloride, ammonium, and NVOC. The open circles indicate sampling wells. (source Kjeldsen *et al.*, 1998a).

hydraulic conductivity and hydraulic gradients showed that pore flow velocities were approximately 50 m yr^{-1} and 10 m yr^{-1} for the Quaternary and Tertiary sandy layers, respectively. A clay layer ~1 m thick located 12 m below ground surface extends over a large part of the landfill. Below this layer there is a more regional micaceous sandy layer ~65 m thick. This layer is vertically limited by another low-permeable clay layer ~80 m below ground surface.

The overall groundwater flow direction is north westerly, but the isopotential contours are semi-circular, indicating a diverging flow. Locally, inside and close to the landfill the flow field shows significant seasonal variation (Figure 12). The reasons for this mounding are not fully understood, but Kjeldsen *et al.* (1998b) suggest three possibilities: (i) higher infiltration in this part of the landfill; (ii) lower hydraulic conductivity in the aquifer underlying this part of the landfill, possibly due to differences in geology, bacterial growth, precipitates, or gas bubbles of methane and carbon dioxide; or (iii) higher infiltration in the borders of the mounding area. The effects of this local mounding are enhanced lateral spreading of the plume, and downward directed hydraulic gradients in the groundwater below the landfill. The latter
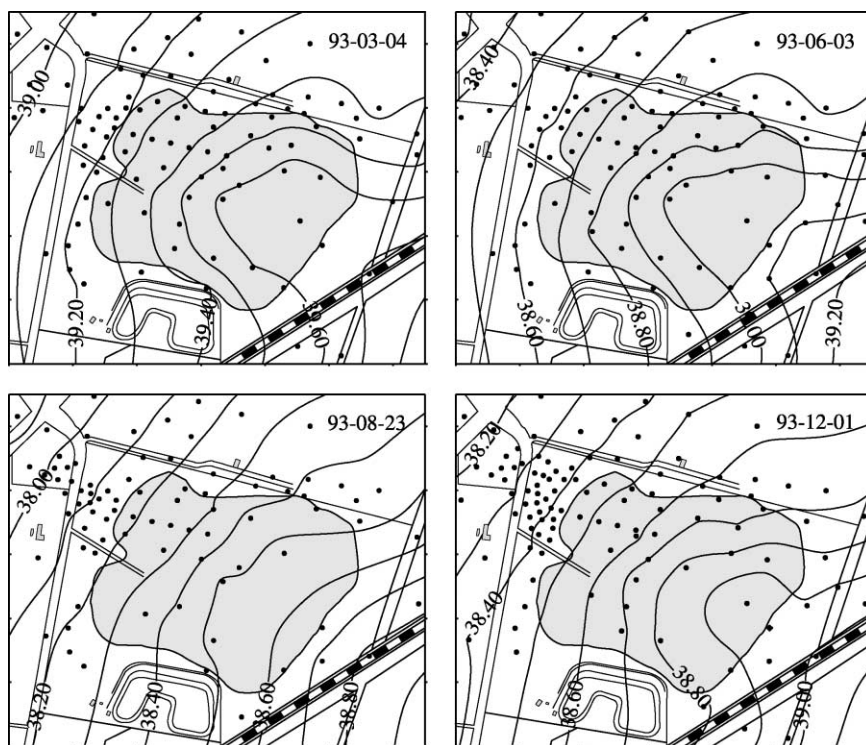
Figure 12 Mounding of the leachate-groundwater table below Grindsted Landfill (DK) shown as isopotential contours for the landfill and surrounding area at four different seasons during 1993 (after Kjeldsen *et al.*, 1998b).

can cause an unexpected vertical spreading pattern, while the enhanced spreading affects the dilution of the plume. Degradation could be increased by enhanced mixing of electron acceptors into the anaerobic parts of the plume. The seasonal variations in the flow field are also important for designing the monitoring network and interpreting the time series monitoring data.

The groundwater quality along the downgradient border of the landfill was mapped in order to illustrate the spreading of leachate into the upper aquifer. Figure 13 shows a three-dimensional sketch of the distribution of chloride, ammonium, and NVOC along the northern and western borders of the landfill as well as the leachate concentrations beneath the landfill.

9.16.7.2 Landfill Leachate Plume

The investigations of the landfill leachate plume at the Grindsted Landfill have been restricted to
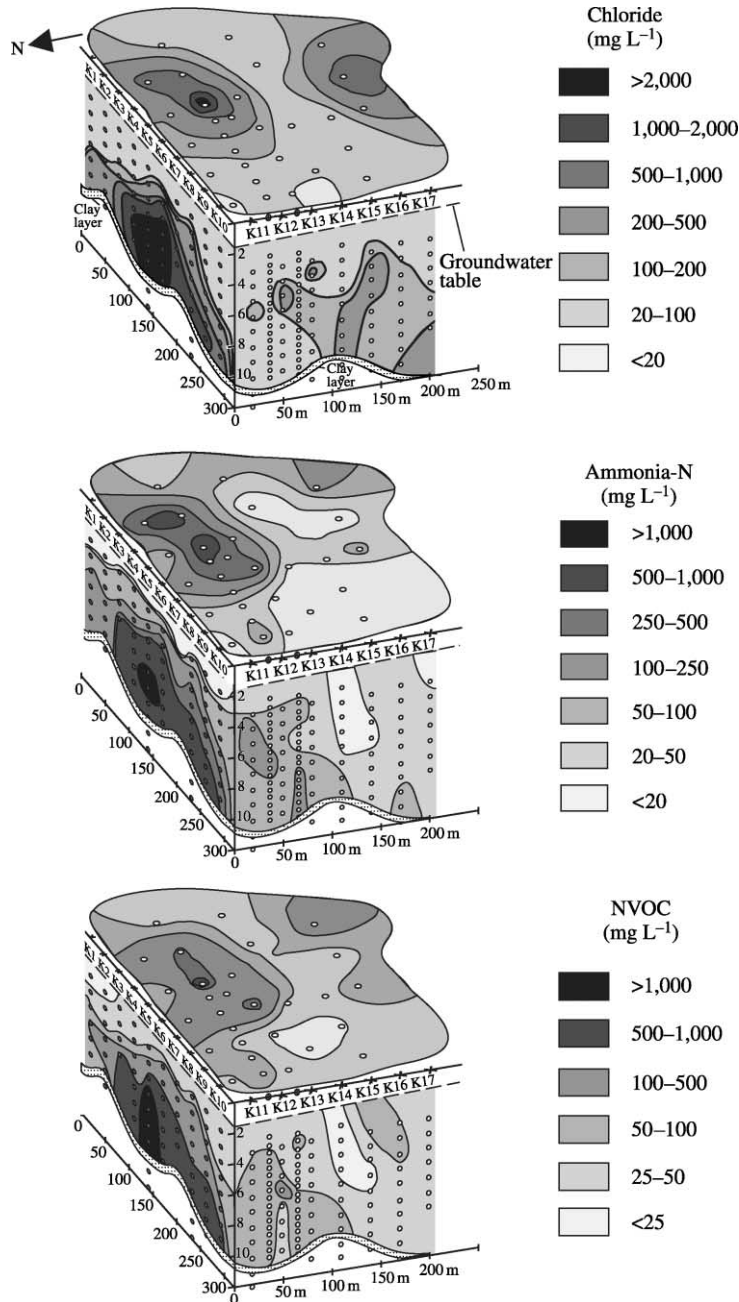
Figure 13 Three-dimensional sketch of leaching pattern for chloride, ammonium, and NVOC from Grindsted Landfill (DK) (source Kjeldsen *et al.*, 1998b).

the upper aquifer (10–12 m) in two transects starting at the western border of the landfill. Transect I (Figure 10) has been characterized in great detail with respect to:

- geology and hydrogeology (Bjerg *et al.*, 1995; Heron *et al.*, 1998; Petersen, 2000);
- inorganic and/or redox-sensitive compounds (Bjerg *et al.*, 1995; Jensen *et al.*, 1998);
- hydrogen levels and *in situ* energetics (Bjerg *et al.*, 1997; Jakobsen *et al.*, 1998);
- aquifer solid composition (Heron *et al.*, 1998);
- microbiology and microbial redox processes (Ludvigsen *et al.*, 1997, 1998, 1999);
- distribution of XOCs (Rügge *et al.*, 1995; Holm *et al.*, 1995); and
- toxicity related to XOCs (Baun *et al.*, 1999, 2000).

Redox environments. At the Grindsted Landfill site, the redox environments were addressed in terms of dissolved redox-sensitive species (Bjerg *et al.*, 1995), aquifer solid compositions (Heron *et al.*, 1998), activity of microorganisms performing each electron-accepting reaction (Ludvigsen *et al.*, 1997), and the concentration of dissolved hydrogen in the groundwater (Jakobsen *et al.*, 1998).
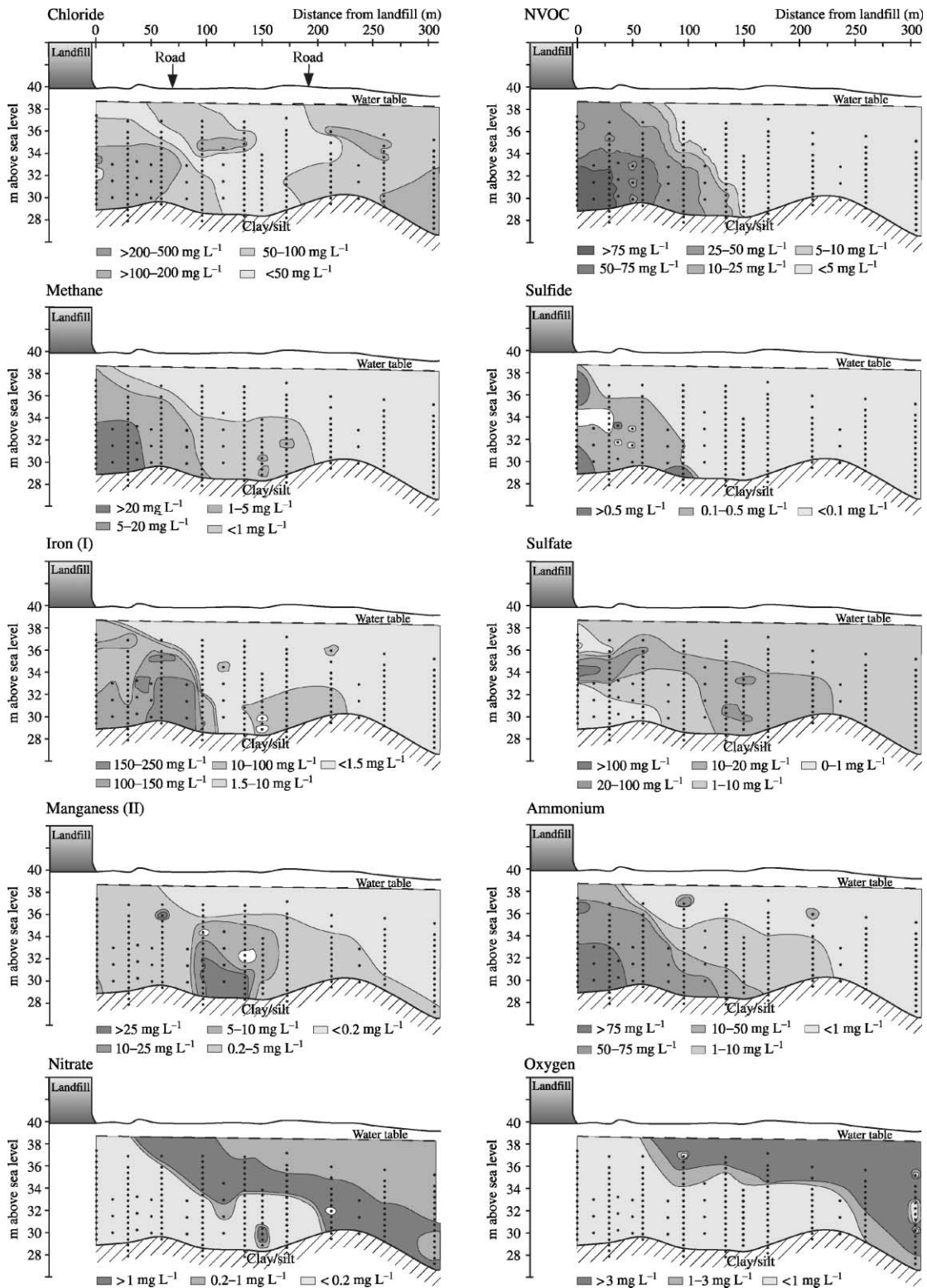
The distribution of dissolved redox-sensitive species (example given in Figure 14) showed that the redox zones were somewhat different in the two parallel vertical transects, which are separated by only 30 m (Figure 15). The overall sequence was consistent with that depicted in Figure 3, although the water chemistry of the Grindsted Landfill (DK) leachate plume suggested that several of the redox zones overlapped. Certainly, the methanogenic and the sulfate-reducing zones overlap (Figure 15). Iron, manganese, and nitrate reducing zones overlap in some cases, but were separated in others. The size of the zones varied considerably between neighboring transects (Bjerg *et al.*, 1995), which is interesting in light of the conclusions drawn earlier for sites for which there are much less data. In this plume methane and ammonium migrate farther than dissolved organic matter (Figure 14), and thus are the dominant reductants at distances greater than 100–150 m from the landfill.

The detailed geological and geochemical description of the aquifer sediment led to an improved understanding of the distribution of iron species in the plume (Heron *et al.*, 1998). The majority of the aquifer consists of mineral-poor fine sands, low in organic matter and iron oxides. Iron and manganese reduction is less important here than at the Vejen Landfill (DK) which is located in the same geographical area, even though very high concentrations of dissolved Fe^{2+} and Mn^{2+} were observed in the Grindsted Landfill (DK) leachate plume. Both a lower initial iron oxide content and a different iron mineralogy (presumably solid grains of crystalline iron oxides) indicated lower iron reactivity.

Bioassays (microbially active, unamended incubations of aquifer solids, and groundwater; Ludvigsen *et al.*, 1998) monitored all the redox processes that occurred and allowed estimates to be made of the rates of the individual redox processes as shown in Figure 16. The rates were fairly low for many of the redox processes. The bioassays also showed that in several samples more than one redox process was significant. However, in most cases one electron acceptor dominated in terms of equivalent rates of organic matter oxidation. Altogether the rates balance fairly well the observed degradation of dissolved organic carbon in the plume. However, the rates determined for denitrification exceeded the dissolved carbon available in that part of the plume suggesting that other electron donors also played a role, perhaps ammonium. It was furthermore demonstrated that low-permeability layers can lead to unexpected redox activities. This was exemplified by the high sulfate reduction activity 170 m from the landfill was caused by localized sulfate and organic-matter-rich deposits, not by leaching from the landfill.

Measurements of dissolved hydrogen have been used to characterize redox levels according to criteria based on the competitive exclusion of terminal electron acceptors for hydrogen oxidation (Lovley and Goodwin, 1988; Chapelle *et al.*, 1995). In the Grindsted Landfill plume, the variations in hydrogen concentration (52 sampling points) were limited, and the values were low (0.004–0.88 nmol L^{-1}) indicating, according to previous criteria, iron-reducing conditions in most of the anaerobic part of the plume (Jakobsen *et al.*, 1998). This was surprising, since the microbial assays and the geochemistry have indicated other active redox processes in the plume (see above). This suggested a need for refining the use of hydrogen in identifying terminal electron acceptors in complex plumes. The hydrogen measurements were used together with the measurements of groundwater chemistry in thermodynamic calculations of free energies of the redox reactions at the temperature of the plume (11 °C). These calculations showed that both sulfate reduction and iron reduction could occur in the plume, since in several places ΔG_r values for each reaction were below a proposed threshold value of -7 kJ mol^{-1} of H_2. Methanogenesis (by CO_2 reduction) showed higher ΔG_r values in all samples, suggesting that methanogenesis only occurs in stagnant pore water, where more reducing conditions may prevail. The small differences in calculated ΔG_r values actually suggested that sulfate reduction and iron

Figure 14 Distribution of Cl$^-$ and dissolved redox-sensitive compounds in Transect 1 downgradient of Grindsted Landfill (DK) (source Bjerg *et al.*, 1995).
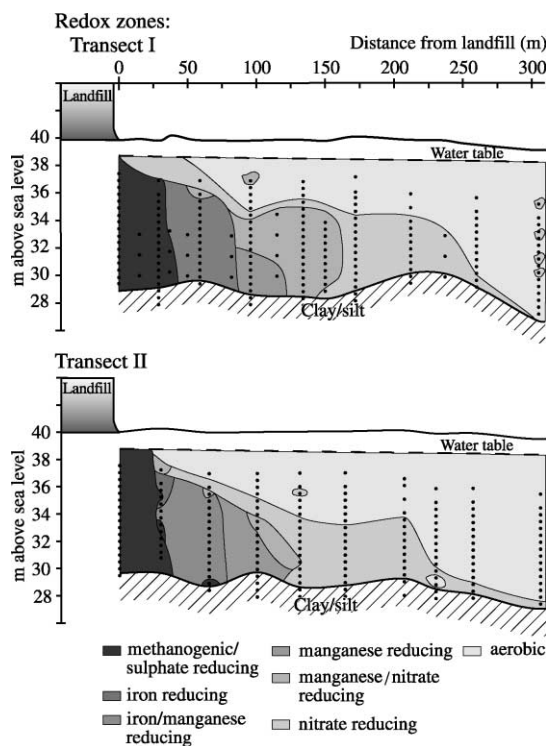
Figure 15 Proposed redox zone distribution in two parallel transect downgradients of Grindsted Landfill (DK) based on the observed groundwater chemistry (source Bjerg *et al.*, 1995).

reduction could take place simultaneously in the same sample.

Overall, this refined use of hydrogen concentrations supported the results of the bioassays and the complex system of redox zones inferred from the distribution of dissolved redox-sensitive species. The Grindsted Landfill (DK) plume is host to all of the proposed redox reactions, but also to secondary oxidation–reduction reactions involving ammonium, methane, manganese oxides, ferrous iron, and sulfides.

Fate of XOCs. The distribution of xenobiotic compounds was mapped in Transect I (Figure 17). More than 15 different organic compounds were identified close to the landfill, with the BTEX compounds dominating. Concentrations of BTEX in the range of $0-222\ \mu g\,L^{-1}$ were observed close to the landfill, with single observations of *o*-xylene concentrations up to $1{,}550\ \mu g\,L^{-1}$ (Rügge *et al.*, 1995). No chlorinated aliphatic compounds were present in this part of the pollution plume. Most of the XOCs were no longer detectable ~ 60 m from the edge of the landfill site. Since dilution and sorption could not account for the disappearance of the xenobiotic compounds, it was proposed that the majority of the xenobiotic compounds in the leachate were transformed under methanogenic/sulfate-reducing or iron-reducing conditions in the aquifer. It should

be emphasized that the apparent attenuation close to the landfill was not based on direct proof, but on a comparison of the actual distribution to the leaching period, dilution, and sorption in the plume. This was convincing for a number of compounds, and was also supported by reactive solute transport modeling (Petersen, 2000). However, benzene shows a distribution that can indicate recalcitrance in the most reduced parts of the plume, but fast disappearance in more oxidized environments (see discussion on benzene in Petersen (2000)). Final conclusions based on field observations may, therefore, be difficult to reach, and may only be feasible where substantial data from different disciplines are available.

The degradation of xenobiotic compounds can also be investigated by microcosm/column experiments and field injection experiments. At the Grindsted Landfill site the degradation of a mixture of xenobiotic compounds (seven aromatic hydrocarbons, four chlorinated aliphatic hydrocarbons, five nitroaromatic hydrocarbons, and two pesticides) was studied using *in situ* microcosms (ISMs) and laboratory microcosms (LMs) (Bjerg *et al.*, 1999; Rügge *et al.*, 1998, 1999a,b). The data from degradation experiments were compared to the field observation data of the aromatic hydrocarbons and we will limit the discussion to these compounds.

An anaerobic stock solution of the XOCs was injected along with bromide as a tracer into five injection wells, installed 15 m downgradient of the landfill. The amount of water injected in the natural gradient experiment was $\sim 5\%$ of the groundwater flux passing the injection wells, yielding approximate concentrations of $75-330\ \mu g\,L^{-1}$ of the XOCs and $100\ mg\,L^{-1}$ of bromide immediately downgradient from the injection wells.

The migration of the compounds was monitored in a dense sampling network consisting of a total of 140 multilevel samplers (1,030 sampling points). Over a period of 924 days, samples were collected from ~ 70 sampling points in the central part of the cloud for the determination of breakthrough curves (BTCs). Degradation and sorption could be determined from the BTCs. After end of the injection, seven cloud snapshots were established covering $\sim 400-700$ sampling points each time. From the snapshot, moment analysis provided an evaluation of the mass loss of solute in the system and the spatial distribution of the cloud in the aquifer. The redox conditions in the studied area of the plume were determined by analysis of water-soluble redox-sensitive compounds sampled every $6-8$ weeks during the experimental period and by groundwater and sediment characterizations combined with microbial assays conducted on sediment and groundwater sampled 800 d after the start of the injection (Albrechtsen *et al.*, 1999).
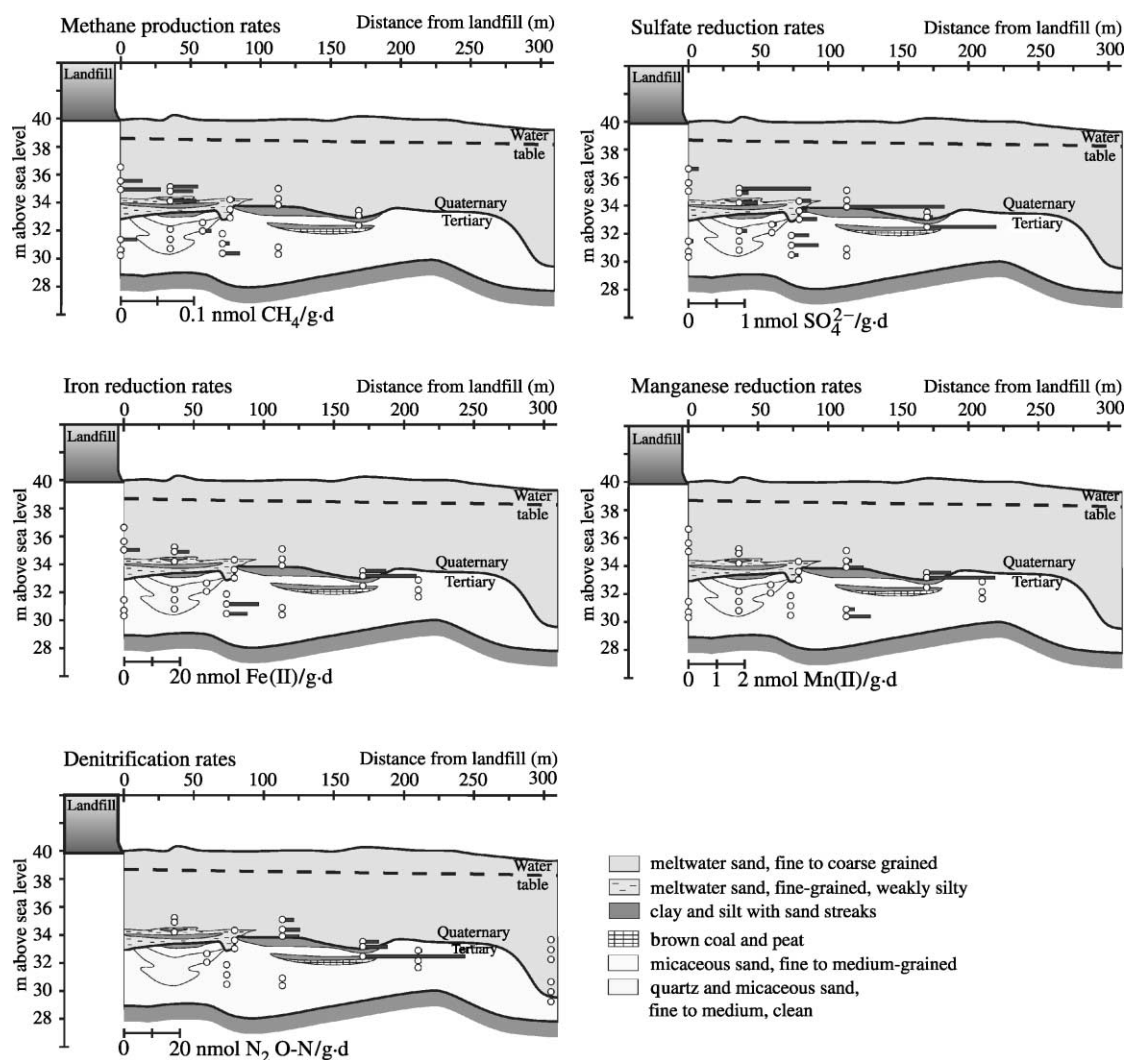
Figure 16 Rates observed by unamended bioassays for individual redox processes at several locations downgradient of Grindsted Landfill (DK) (Ludvigsen *et al.*, 1998).

In the injection experiment, complete degradation of toluene was observed within the most reduced part of the aquifer where iron reduction, sulfate reduction, and methanogenesis occurred. Partial degradation of *o*-xylene was observed. The degradation of *o*-xylene was not initiated before the cloud had reached the part of the aquifer where iron reduction was predominant. Examples of the cloud movement after 649 d are given in Figure 18. Benzene was not degraded within the experimental period of 924 d. Due to highly varying background concentrations, it was not possible to determine whether any degradation of the compounds ethylbenzene and *m/p*-xylene had occurred.

In parallel with the anaerobic field injection experiment, ISMs were installed at five locations downgradient of the landfill (see Nielsen *et al.* (1996) for description of this technique). Also, laboratory batch experiments (LBs) were conducted with sediment and groundwater from the corresponding locations. The experimental periods of the ISMs and the LBs were up to 220 d and 537 d, respectively. Both systems involved the same mixture of 18 compounds (Bjerg *et al.*, 1999). For the aromatic compounds only toluene was degraded in the ISM, while also *o*- and *m/p*-xylene was degraded in the LB. Benzene, ethylbenzene and naphthalene were not degraded in either the ISM or the LB.

In general, good agreement was observed between the results obtained in the injection experiment, the ISMs, and the LBs; however, a few differences were found, as shown in Table 5. These differences were mainly due to the different experimental periods, 924 d in the injection experiment, and up to 210 d and 537 d in the ISMs and LBs, respectively. However, differences between the static and flow systems also influenced the results. This comparison indicated

Grindsted Landfill: redox zones   Distance from landfill (m)

Grindsted Landfill: xylenes
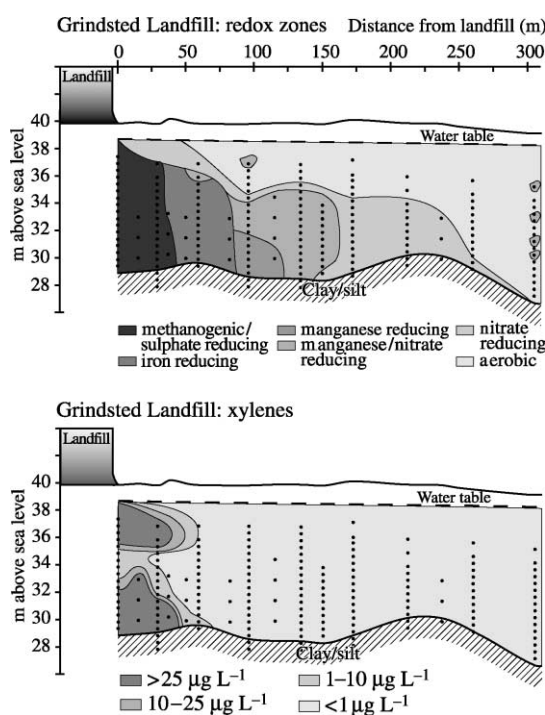
Figure 17 Proposed redox zonation, and distribution of xylenes in Transect I at the downgradient of Grindsted Landfill (DK) (after Bjerg *et al.*, 1995; Rügge *et al.*, 1995).

that the ISM is a good method for studying degradation in the field for compounds with lag periods shorter than 50–100 d. LBs are also a useful and cost-saving approach for studying degradation. The batch setup allows for very long experimental periods. Therefore, the LBs are useful for mixtures of compounds with both shorter and longer lag periods as well as for compounds with varying degradation rates. The results on degradation, however, have been obtained for rather simple compounds, and it is not known how well the batch experiments mimic the field situation for more complex compounds.

The experiments carried out in the anaerobic part of the leachate plume indicate that natural attenuation of toluene and *o*-xylene takes place close to landfill. However, the results for ethylbenzene do not agree with the plume observations. In the case of benzene the degradation may take place at a longer distance from the landfill in more oxidized environments (Petersen, 2000).

In summary, a description of natural attenuation processes for XOCs in a landfill leachate is not an easy task and may require a number of approaches including field observations, experiments in the laboratory and field and also reactive solute transport modeling. The latter is an important

tool for integrating data bearing on geology and hydrogeology, redox conditions, distribution of xenobiotic compounds, and degradability/degradation rates.

9.16.8 ENVIRONMENTAL RESTORATION

9.16.8.1 Monitored Natural Attenuation

Natural attenuation refers to processes that naturally transform contaminants to less harmful forms or immobilize contaminants so that they are less of a threat to the environment; see *Natural Attenuation for Groundwater Remediation* by the National Research Council (2000). This includes: dispersion/dilution, sorption, volatilization, and degradation (abiotic, biotic).

Degradation is the most interesting process, because the contaminants can be transformed into less harmful products (carbon dioxide and water). Engineered application of natural attenuation processes as a remedy is termed monitored natural attenuation (MNA, see US EPA). This involves a monitoring component in addition to an evaluation of the natural attenuation processes.

The results from the landfill sites reviewed here indicate a significant potential for natural attenuation of XOCs at landfills sites. There are as of early 2000s, however, only a few examples, compared to the number of landfills around the world. Additional well-documented field examples are badly needed. Experience from more landfill sites will also help in developing procedures for demonstrating natural attenuation, which is not a straightforward procedure. The experience presented in this chapter and the evaluation of natural attenuation as a remedy at landfill sites by Christensen *et al.* (2000a) suggest that five points will be critical:

- local hydrogeological conditions in the landfill area may affect the spreading of the contaminants;
- the size of the landfill and the heterogeneity of the source may create a variable leaching pattern and multiple plumes;
- the complexity of leachate plumes with respect to compounds (inorganic, XOCs) and biogeochemical processes may be an obstacle;
- the time frame of leaching from a landfill site is apt to be very long and will call for long-term evaluation of the attenuation capacity; and
- demonstration of natural attenuation in terms of mass reduction at the field scale is difficult.

The importance of each issue will depend on the actual landfill. It should also be emphasized that even though these problems may be difficult to solve, very few alternatives exist for remediation at landfill sites (see next section).
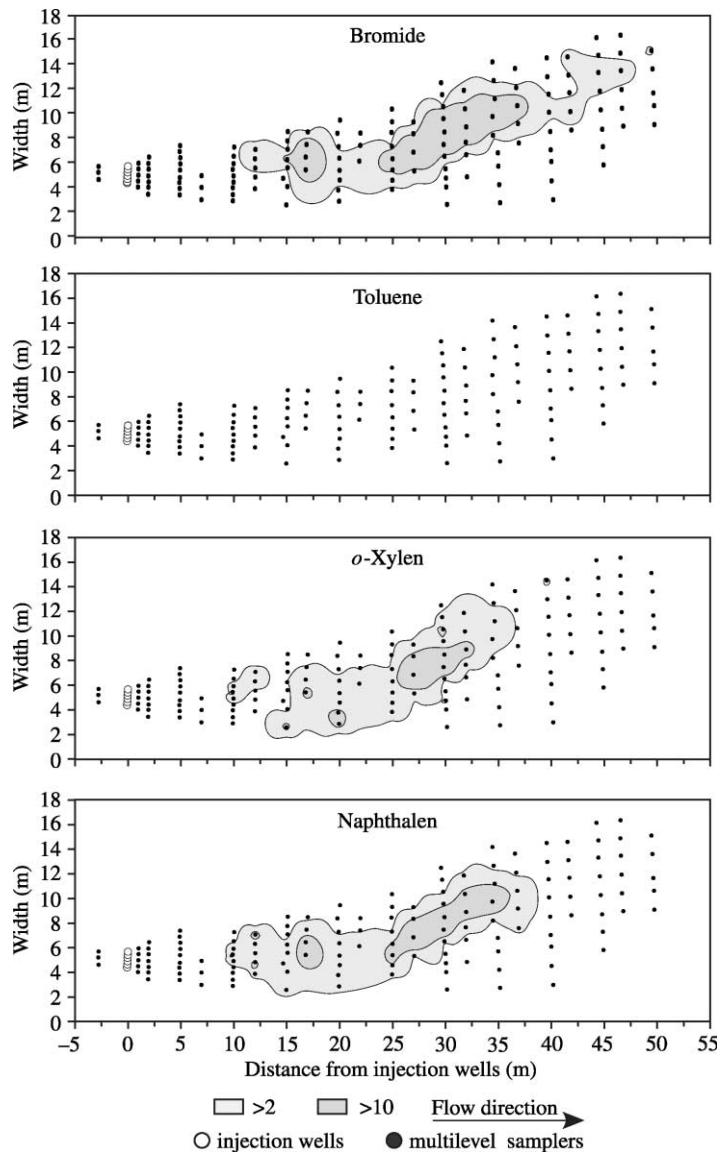
Figure 18 Observed clouds of bromide, toluene, *o*-xylene, naphthalene after 649 d. Bromide in g m^{-2}, xenobiotics in mg m^{-2} (source Rügge *et al.*, 1999a).

9.16.8.2 Engineered or Enhanced Remediation

Remediation of landfill leachate plumes has, in most cases, focused on source control. This is due to the fact that landfills are so large that the mass of pollutants contained in the landfill body would be able to sustain the leachate plume for centuries making a remedy focusing on the plume a long and costly approach. Additional reasons for focusing on the source are that the landfill also may be a "time bomb" containing chemical waste in drums subject to corrosion, landfill gas emission needs to be controlled, improvements of landscape value is requested by the community, and potentially new landfilling capacity is in demand.

Source controls may involve the following.

• Excavation in order to remove drums and highly polluted waste. If the most contaminated waste in the landfill body can be identified, excavation may be an efficient remediation technique. Partly corroded drums may be difficult to handle without contaminating the waste material; this is for precautions and care. The excavated material may be removed for off-site treatment or may be re-landfilled in landfill sections established with landfill liners, leachate drainage collection, and treatment systems.

• Sheet piling in order to control groundwater migration into and out of the waste if waste

Table 5 Potential for degradation of the aromatic compounds in anaerobic leachate affected groundwater at Grindsted Landfill (DK).

Grindsted Landfill	Benzene	Toluene	Ethyl-benzene	m/p-Xylene	o-Xylene	Naphthalene
(1) Field Injection 15–45 m	−	+	?	?	−	−
(1) Field Injection 45–65 m	−	+	?	?	+	−
(2) ISM and LB						
LB (I) 15 m	−	+	−	−	−	−
LB (II) 15 m	−	+	−	−	−	−
LB (II) 25 m	−	+	−	−	−	−
ISM 25 m	−	−	−	−	−	−
LB (II) 35 m	−	−	−	−	−	−
ISM 35 m	−	−	−	−	−	−
LB (II) 45 m	−	+	−	−	−	−
ISM 45 m	−	−	−	−	−	−
LB (II) 55 m	−	+	−	+	−	−
ISM 55 m	−	+	−	−	−	−
LB (I) 60 m	−	+	−	+	+	−

(1) Rügge *et al.* (1999a) and (2) Bjerg *et al.* (1999). +, degradation observed. −, no degradation observed. ?, not possible to determine due to highly varying background conditions.

exists below the groundwater table. The sheet piles should reach low-permeable strata. This approach is, therefore, limited to fairly shallow aquifers. Sheeting piling can effectively reduce the exchange of leachate-contaminated groundwater with the surrounding flow of groundwater. However, sufficient control can only be obtained with this approach if it is combined with continuous removal of leachate-contaminated groundwater from the sheet-piled area. This will create groundwater seepage into the leachate-contaminated area instead of leachate migration out of the area.

- Impermeable top covers in terms of plastic liners or clay membranes can be installed in order to prevent water infiltration into the waste and hence cease leachate generation for waste landfilled above the seasonal water table. Top covers are relatively expensive to install and maintenance must be expected in perpetuity. Adequate surface water removal is important to limit the infiltration through cracks, fractures, or pinholes in the liners. Vegetation is often introduced to improve landscape value but requires special measures to avoid root penetration of the membranes.
- In-landfill treatments have been used in a few experimental cases including aerating the landfill body through vertical wells installed in the central part of the landfill body and extracting the off-gases through collection wells placed in the periphery of the landfill (Heyer *et al.*, 2001). The approach is a combined stripping system for methane and volatile organics and a composting system providing oxygen to the microbial processes in the landfill body. The approach may reduce the contaminant level of the leachate, but most likely will not eliminate

leachate generation when aeration is terminated.
- Pump-and-treat systems can be installed to remove contaminated groundwater from areas, beneath the landfill. This will control the migration of the leachate away from the landfill but the pump-and-treat system must be maintained as long as the landfill is a threat to the groundwater. Pump and treat at source is not very different than that in the leachate plume except that the volume is likely to be less and the concentrations of contaminants are likely to be higher when used for source control.

Engineered remediations of leachate plumes are few and mainly involve pump-and-treat schemes. Since leachate plumes may contain a broad spectrum of contaminants potentially with an uneven distribution in the plume, any remediation scheme must be broadly targeted and robust. This supports pump and treat as a suitable candidate.

The number of landfill plumes that have been remediated are very few compared to, for example, plumes with chlorinated solvents and hydrocarbons, and the remediation of leachate plumes has usually involved a combination of approaches focusing on the source remediation and monitored natural attenuation for the plume.

9.16.9 FUTURE CHALLENGES AND RESEARCH TOPICS

The number of detailed landfill studies has been quite limited. A few sites have been characterized to a high degree (including Banisveld Landfill, Borden Landfill, Grindsted Landfill, Norman Landfill, and Vejen Landfill) by using multidisciplinary approaches. These studies

consistently show the importance of integrated studies in order to understand the biogeochemical processes in landfill leachate plumes. The results presented in this chapter have revealed a number of topics where research using similar approaches could be beneficial. Suggestions for future challenges and research topics are listed below:

- *Source and spreading of landfill leachate.* Density flow is most likely at landfill sites, but the current understanding of instability effects and our ability to predict the impact of density flow under field conditions is poor. Also, the reasons for the often observed mounding of the groundwater table beneath landfills are not fully understood and need more attention.

- *Biogeochemical processes.* A good conceptual understanding of the biogeochemical processes in landfill leachate plumes exists and the overall understanding of redox processes is good. The challenge is to quantify rates and capacity, so that the relative importance of core processes (e.g., microbial iron reduction capacity) and fringe processes (mixing of electron acceptors) can be evaluated in order to predict the long-term behavior of the plume. Application of stable isotope as well as molecular techniques may be useful in such studies, but simple model/mass balance approaches or advanced multidimensional reactive solute transport models are also needed to integrate flow, transport, and reactive processes.

- *Fate of XOCs.* Significant degradation of XOC has been demonstrated at most landfill sites, but discrepancies between field observations and experimental work have been observed. Lack of knowledge of the expected fate is mainly related to "new" compounds such as pesticides, pharmaceuticals, and phthalates. However, the discrepancies also reveal that the methods used for documentation of natural attenuation processes are poor in landfill leachate plumes. Recent studies have suggested using probe compounds as tracers, degradation products, stable isotopes, and enantiomeric ratios, but these methods are all quite new and need to be improved before they can be applied in practice for documenting natural attenuation. Flux approaches have been suggested for quantification of mass removal for XOCs; however, current applications indicate that this is a costly and complex approach, which needs refinement.

- *Remediation of landfill leachate* plumes has been performed only in very few cases. The most promising technique is monitored natural attenuation, but guidelines and practical experience are necessary to ensure proper implementation. The need for monitoring and the length of the monitoring period of landfills of different lifetimes *in situ* very much a matter of discussion.

REFERENCES

Acton D. W. and Barker J. F. (1992) *In situ* biodegradation potential of aromatic hydrocarbons in anaerobic groundwater. *J. Contamin. Hydrol.* **9**, 325–352.

Adams E. E. and Gelhar L. W. (1992) Field study in a heterogeneous aquifer: 2. Spatial moments analysis. *Water Resour. Res.* **28**, 3293–3307.

Albrechtsen H.-J. and Christensen T. H. (1994) Evidence for microbial iron reduction in a landfill leachate-polluted aquifer (Vejen, Denmark). *Appl. Environ. Microbiol.* **60**, 3920–3925.

Albrechtsen H.-J., Bjerg P. L., Ludvigsen L., Rügge K., and Christensen T. H. (1999) An anaerobic field injection experiment in a landfill leachate plume (Grindsted, Denmark): 2. Deduction of anaerobic (methanogenic, sulfate and Fe(III)reducing) redox conditions. *Water Resour. Res.* **35**, 1247–1256.

Albrechtsen H.-J., Mills M., Aamand J., and Bjerg P. L. (2001) Degradation of herbicides in shallow Danish aquifers—an integrated laboratory and field study. *Pest Manage. Sci.* **57**, 341–350.

Allen-King R. M., Gillham R. W., and Barker J. F. (1996) Fate of dissolved toluene during steady infiltration through unsaturated soil: I. Method emphasizing chloroform as a volatile, sorptive, and recalcitrant tracer. *J. Environ. Qual.* **25**, 279–286.

Arneth J.-D., Milde G., Kerndorff H., and Schleyer R. (1989) Waste deposit influences on groundwater quality as a tool for waste type and site selection for final storage quality. In *The Landfill*, Lecture Notes in Earth Sciences (ed. P. Baccini). Springer, Berlin, vol. 20, pp. 399–424.

Assmuth T. W. and Strandberg T. (1993) Ground-water contamination at Finnish landfills. *Water Air Soil. Pollut.* **69**, 179–199.

Barker J. F., Tessmann J. S., Plotz P. E., and Reinhard M. (1986) The organic geochemistry of a sanitary landfill leachate plume. *J. Contamin. Hydrol.* **1**, 171–189.

Baun A., Kløft L., Bjerg P. L., and Nyholm N. (1999) Toxicity testing of organic chemicals in groundwater polluted with landfill leachate. *Environ. Toxicol. Chem.* **18**, 2046–2056.

Baun A., Jensen S. D., Bjerg P. L., Christensen T. H., and Nyholm N. (2000) Toxicity of organic chemical pollution in groundwater downgradient of a landfill (Grindsted, Denmark). *Environ. Sci. Technol.* **34**, 1647–1652.

Baun A., Ask L., Ledin A., Christensen T. H., and Bjerg P. L. (2003) Natural attenuation of xenobiotic organic compounds in a landfill leachate plume (Vejen, Denmark). *J. Contamin. Hydrol.* **65**, 269–291.

Beeman R. E. and Suflita J. M. (1987) Microbial ecology of a shallow unconfined ground water aquifer polluted by municipal landfill leachate. *Microb. Ecol.* **14**, 39–54.

Beeman R. E. and Suflita J. M. (1990) Environmental factors influencing methanogenesis in a shallow anoxic aquifer: a field and a laboratory study. *J. Ind. Microb.* **5**, 45–58.

Belevi H. and Baccini P. (1992) Long-term leachate emissions from municipal solid waste landfills. In *Landfilling of Waste: Leachate* (eds. T. H. Christensen, R. Cossu, and R. Stegmann). Elsevier, London, pp. 431–440.

Beller H. (2000) Metabolic indicators for detecting *in situ* anaerobic alkaylbenzene degradation. *Biodegradation* **11**, 125–139.

Bisdom E. B. A., Boekestein A., Curmi P., Legas P., Letsch A. C., Loch J. P. G., Nauta R., and Wells C. B. (1983) Submicroscopy and chemistry of heavy metal contaminated precipitates from column experiments simulating conditions in a soil beneath a landfill. *Geoderma* **30**, 1–20.

Bjerg P. L., Rügge K., Pedersen J. K., and Christensen T. H. (1995) Distribution of redox sensitive groundwater quality parameters downgradient of a landfill (Grindsted, Denmark). *Environ. Sci. Technol.* **29**, 1387–1394.

Bjerg P. L., Jakobsen R., Bay H., Rasmussen M., Albrechtsen H.-J., and Christensen T. H. (1997) Effects of sampling well construction on H_2 measurements made for characterization of redox conditions in a contaminated aquifer. *Environ. Sci. Technol.* **31**, 3029–3031.

Bjerg P. L., Rügge K., Cortsen J., Nielsen P. H., and Christensen T. H. (1999) Degradation of aromatic and chlorinated aliphatic hydrocarbons in the anaerobic part of the Grindsted Landfill leachate plume: *in situ* microcosm and laboratory batch experiments. *Ground Water* **37**, 113–121.

Bradley P. M. (2000) Microbial degradation of chloroethenes in groundwater systems. *Hydrogeol. J.* **8**, 104–111.

Breit G. N., Cozzarelli I. M., Johnson R. D., and Norvell J. S. (1996) Interaction of alluvial sediments and a leachate plume from a landfill near Norman Oklahoma. *Geol. Soc. Am. Abstr. Prog.* **28**(7), A258.

Broholm M. M., Rügge K., Tuxen N., Højbjerg A. L., Mosbæk H., and Bjerg P. L. (2001) Fate of herbicides in a shallow aerobic aquifer: a continuous field injection experiment (Vejen, Denmark). *Water Resour. Res.* **37**, 3163–3176.

Brun A., Engesgaard P., Christensen T. H., and Rosbjerg D. (2002) Modelling of transport and biogeochemical processes in pollution plumes: Vejen Landfill, Denmark. *J. Hydrol.* **256**, 228–248.

Chapelle F. H. and Bradley P. M. (1998) Selecting remediation goals by assessing the natural attenuation capacity of groundwater systems. *Bioremed. J.* **2**, 227–238.

Chapelle F. H., McMahon P. B., Dubrovsky N. M., Fujii R. F., Oaksford E. T., and Vroblesky D. A. (1995) Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems. *Water Resour. Res.* **31**, 359–371.

Christensen T. H. and Kjeldsen P. (1989) Basic biochemical processes in landfills. In *Sanitary Landfilling: Process, Technology and Environmental Impact* (eds. T. H. Christensen, R. Cossu, and R. Stegmann). Academic Press, London, chap. 2.1, pp. 29–49.

Christensen T. H., Kjeldsen P., Albrechtsen H.-J., Heron G., Nielsen P. H., Bjerg P. L., and Holm P. E. (1994) Attenuation of landfill leachate pollutants in aquifers. *Crit. Rev. Environ. Sci. Technol.* **24**, 119–202.

Christensen J. B., Jensen D. L., and Christensen T. H. (1996) Effect of dissolved organic carbon on the mobility of cadmium, nickel, and zinc in leachate polluted groundwater. *Water Res.* **30**, 3037–3049.

Christensen T. H., Bjerg P. L., and Kjeldsen P. (2000a) Natural attenuation: a feasible approach to remediation of groundwater pollution at landfills? *GWMR* **20**(1), 69–77.

Christensen T. H., Bjerg P. L., Banwart S., Jakobsen R., Heron G., and Albrechtsen H.-J. (2000b) Characterization of redox conditions in groundwater contaminant plumes. *J. Contamin. Hydrol.* **45**, 165–241.

Christensen T. H., Kjeldsen P., Bjerg P. L., Jensen D. L., Christensen J. B., Baun A., Albrechtsen H.-J., and Heron G. (2001) Biogeochemistry of landfill leachate plumes. *Appl. Geochem.* **16**, 659–718.

Cozzarelli I. M., Suflita J. M., Ulrich G. A., Harris S. H., Scholl M. A., Schlottmann J. L., and Christenson S. (2000) Geochemical and microbiological methods for evaluating anaerobic processes in an aquifer contaminated by landfill leachate. *Environ. Sci. Technol.* **34**, 4025–4033.

DeWalle F. B. and Chian S. K. (1981) Detection of trace organics in well near solid waste landfill. *AWWA J.* **73**, 206–211.

Eganhouse R. P., Dorsey T. F., Phinney C. S., and Westcott A. M. (1996) Processes affecting the fate of monoaromatic hydrocarbons in an aquifer contaminated by crude oil. *Environ. Sci. Technol.* **30**, 3304–3312.

Eganhouse R. P., Cozzarelli I. M., Scholl M. A., and Matthews L. L. (2001) Natural attenuation of volatile organic compounds (VOCs) in the leachate plume of a municipal landfill: using alkylbenzenes as a process probe. *Ground Water* **39**, 192–202.

Freeze R. A. and Cherry J. A. (1979) *Groundwater.* Prentice Hall, Englewood Cliffs, NJ.

Gelhar L. W., Welty C., and Rehfeldt K. R. (1992) A critical review of data on field-scale dispersion in aquifers. *Water Resour. Res.* **28**, 1955–1974.

Grbic-Galic D. (1990) Methanogenic transformation of aromatic hydrocarbons and phenols in groundwater aquifers. *Geomicrobiol. J.* **8**, 167–200.

Hackley K. C., Liu C. L., and Coleman D. D. (1996) Environmental isotope characteristics of landfill leachates and gases. *Ground Water* **34**, 827–836.

Harris S. H., Ulrich G. A., and Suflita J. M. (1999) *Dominant Terminal Electron Accepting Processes Occuring at a Landfill Leachate-impacted Site as Indicated by Field and Laboratory Measurements.* US Geological Survey Water Resources Investigations Report #99-4018C, Reston, VA.

Heider J., Spormann A. M., Beller H. R., and Widdel F. (1999) Anaerobic bacterial metabolism of hydrocarbons. *FEMS Microbiol. Rev.* **22**, 459–473.

Heron G. (1994) Redox buffering in landfill leachate contaminated aquifers. PhD Thesis, Department of Environmental Science and Engineering, Technical University of Denmark, Lyngby.

Heron G. and Christensen T. H. (1995) Impact of sediment-bound iron on redox buffering in a landfill leachate polluted aquiffer (Vejen, Denmark). *Environ. Sci. Technol.* **29**, 187–192.

Heron G., Christensen T. H., and Tjell J. C. (1994a) Oxidation capacity of aquifer sediments. *Environ. Sci. Technol.* **28**, 153–158.

Heron G., Crouzet C., Bourg A. C. M., and Christensen T. H. (1994b) Speciation of Fe(II) and Fe(III) in contaminated aquifer sediments using chemical extraction techniques. *Environ. Sci. Technol.* **28**, 1698–1705.

Heron G., Bjerg P. L., Gravesen L., Ludvigsen L., and Christensen T. H. (1998) Geology and sediment geochemistry of a landfill leachate contaminated aquifer (Grindsted, Denmark). *J. Contamin. Hydrol.* **29**, 301–317.

Heyer K.-U., Hupe K., Ritzkowski M., and Stegmann R. (2001) Technical implementation an operation of the low pressure aeration of landfills. In *Sardinia 2001: 8th International Waste Management and Landfill Symposium, October 1–5, Sardinia, Italy,* Proceedings Vol. IV (eds. T. H. Christensen, R. Cossu, and R. Stegmann). CISA, Cagliari, Italy.

Holliger C., Wohkfahrt G., and Diekert G. (1999) Reductive dechlorination in the energy metabolism of anaerobic bacteria. *FEMS Microbiol. Rev.* **22**, 383–398.

Holm J. V., Rügge K., Bjerg P. L., and Christensen T. H. (1995) Occurrence and distribution of pharmaceutical organic compounds in the groundwater downgradient of a landfill (Grindsted, Denmark). *Environ. Sci. Technol.* **29**, 1415–1420.

Istok J. D., Humphrey M. D., Schroth M. H., Hyman M. R., and O'Reilly K. T. (1997) Single-well "push–pull" test for *in situ* determination of microbial activities. *Ground Water* **35**, 619–631.

Jakobsen R., Albrechtsen H.-J., Rasmussen M., Bay H., Bjerg P. L., and Christensen T. H. (1998) H_2 concentrations in a landfill leachate plume (Grindsted, Denmark): *in situ* energetics of terminal electron acceptor processes. *Environ. Sci. Technol.* **32**, 2142–2148.

Jensen K. H., Bitsch K., and Bjerg P. L. (1993) Large-scale dispersion experiments in a sandy aquifer in Denmark: observed tracer movements and numerical analysis. *Water Resour. Res.* **29**, 673–696.

Jensen D. L., Boddum J. K., Redemann S., and Christensen T. H. (1998) Speciation of dissolved iron(II) and manganese(II) in a groundwater pollution plume. *Environ. Sci. Technol.* **32**, 2657–2664.

Jensen D. L., Boddum J. K., Tjell J. C., and Christensen T. H. (2002) The solubility of rhodochrosite ($MnCO_3$) and siderite ($FeCO_3$) in anaerobic aquatic environments. *Appl. Geochem.* **17**, 503–511.

Johnston J. J., Borden R. C., and Barlaz M. A. (1996) Anaerobic biodegradation of alkylbenzene and trichloroetylene in aquifer sediment downgradient of a sanitary landfill. *J. Contamin. Hydrol.* **23**, 263–283.

Jones E. J. P., Deal A., Lorah M. M., Kirshtein J. D., and Voytek M. A. (2002) The effect of Fe(III) on microbial degradation of chlorinated volatile organic compounds in a contaminated freshwater wetland. In *102nd General Meeting of the American Society for Microbiology, Salt Lake City, UT, May 19–23*. American Society for Microbiology, Washington, DC.

Kehew A. E., Schwindt F. J., and Brown D. J. (1984) Hydrogeochemical interaction between a municipal waste stabilization lagoon and a shallow aquifer. *Groundwater* **22**, 746–754.

Kjeldsen P. (1986) Attenuation of landfill leachate in soil and aquifer material. PhD Thesis, Department of Environmental Engineering, Technical University of Denmark, Lyngby.

Kjeldsen P. (1993) Groundwater pollution source characterization of an old landfill. *J. Hydrol.* **142**, 349–371.

Kjeldsen P. and Christophersen M. (2001) Composition of leachate from old landfills in Denmark. *Waste Manage. Res.* **19**, 249–256.

Kjeldsen P., Kjølholt J., Schultz B., Christensen T. H., and Tjell J. C. (1990) Sorption and degradation of chlorophenols, nitrophenols and organophosphorus pesticides in the subsoil under landfills—laboratory studies. *J. Contamin. Hydrol.* **6**, 165–184.

Kjeldsen P., Grundtvig A., Winther P., and Andersen J. S. (1998a) Characterization of an old municipal landfill (Grindsted, Denmark) as a groundwater pollution source: landfill history and leachate composition. *Waste Manage. Res.* **16**, 3–13.

Kjeldsen P., Bjerg P. L., Rügge K., Christensen T. H., and Pedersen J. K. (1998b) Characterization of an old municipal landfill (Grindsted, Denmark) as a groundwater pollution source: landfill hydrology and leachate migration. *Waste Manage. Res.* **16**, 14–22.

Kjeldsen P., Barlaz M. A., Rooker A. P., Baun A., Ledin A., and Christensen T. H. (2002) Present and long term composition of MSW landfill leachate—a review. *Crit. Rev. Environ. Sci. Technol.* **32**, 297–336.

Larsen T., Christensen T. H., Pfeffer F. M., and Enfield C. G. (1992) Landfill leachate effects on sorption of organic micropollutants onto aquifer materials. *J. Contamin. Hydrol.* **9**, 307–324.

Lorah M. M. and Olsen L. D. (1999a) Degradation of 1,1,2,2-tetrachloroethane in a freshwater tidal wetland: field and laboratory evidence. *Environ. Sci. Technol.* **33**, 227–234.

Lorah M. M. and Olsen L. D. (1999b) Natural attenuation of chlorinated volatile organic compounds in a freshwater tidal wetland: field evidence of anaerobic biodegradation. *Water Resour. Res.* **35**, 3811–3827.

Lorah M. M., Voytek M. A., Kirshtein J. D., and Jones E. J. *Anaerobic Degradation of 1,1,2,2-Tetrachloroethane and Association with Microbial Communities in a Freshwater Tidal Wetland, Aberdeen Proving Ground, Maryland: Laboratory Experiments and Comparisons to Field Data.* US Geological Survey Water-Resources Investigations Report 02-4157 (in press).

Lovley D. R. (1991) Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiol. Rev.* **55**, 259–287.

Lovley D. R. and Goodwin S. (1988) Hydrogen concentrations as an indicator of the predominant terminal electron-accepting reactions in aquatic sediments. *Geochim. Cosmochim. Acta* **52**, 2993–3003.

Ludvigsen L., Albrechtsen H.-J., Holst H., and Christensen T. H. (1997) Correlating phospholipid fatty acids (PLFA) in a landfill leachate polluted aquifer with biogeochemical factors by multivariate statistical methods. *FEMS Microbiol. Rev.* **20**, 447–460.

Ludvigsen L., Albrechtsen H.-J., Heron G., Bjerg P. L., and Christensen T. H. (1998) Anaerobic microbial redox processes in a landfill leachate contaminated aquifer (Grindsted, Denmark). *J. Contamin. Hydrol.* **33**, 273–291.

Ludvigsen L., Albrechtsen H.-J., Ringelberg D. B., Ekelund F., and Christensen T. H. (1999) Composition and distribution of mirobial biomass in a landfill leachate contaminated aquifer (Grindsted, Denmark). *Microbiol. Ecol.* **37**, 197–207.

Lyngkilde J. and Christensen T. H. (1992a) Fate of organic contaminants in the redox zones of a landfill leachate pollution plume (Vejen, Denmark). *J. Contamin. Hydrol.* **10**, 291–307.

Lyngkilde J. and Christensen T. H. (1992b) Redox zones of a landfill leachate pollution plume (Vejen, Denmark). *J. Contamin. Hydrol.* **10**, 273–289.

MacFarlane D. S., Cherry J. A., Gillham R. W., and Sudicky E. A. (1983) Migration of contaminants in groundwater at a landfill: a case study. 1. Groundwater flow and plume delineation. *J. Hydrol.* **63**, 1–29.

McGuire J. T., Smith E. W., Long D. T., Hyndman D. W., Haack S. K., Klug M. J., and Velbel M. A. (2000) Temporal variations in parameters reflecting terminal-electron-accepting processes in an aquifer contaminated with waste fuel and chlorinated solvents. *Chem. Geol.* **169**, 471–485.

McGuire J. T., Long D. T., Klug M. J., Haack S. K., and Hyndman D. W. (2002) Evaluating behavior of oxygen, nitrate, and sulfate during recharge and quantifying reduction rates in a contaminated aquifer. *Environ. Sci. Technol.* **36**, 2693–2700.

Murray J., Rouse J. V., and Carpenter A. B. (1981) Groundwater contamination by sanitary landfill leachate and domestic wastewater in carbonate terrain: principal source diagnosis, chemical transport characteristics and design implications. *Water Res.* **15**, 745–757.

National Research Council (2000) *Natural Attenuation for Groundwater Remediation*. National Academy Press, Washington, DC, 274pp.

Nicholson R. V., Cherry J. A., and Reardon E. J. (1983) Migration of contaminants in groundwater at a landfill: a case study. 6. Hydrogeochemistry. *J. Hydrol.* **63**, 131–176.

Nielsen P. H., Albrechtsen H.-J., Heron G., and Christensen T. H. (1995a) *In situ* and laboratory studies on the fate of specific organic compounds in an anaerobic landfill leachate plume: I. Experimental conditions and fate of phenolic compounds. *J. Contamin. Hydrol.* **20**, 27–50.

Nielsen P. H., Bjarnadottir H., Winter P. L., and Christensen T. H. (1995b) *In situ* and laboratory studies on the fate of specific organic compounds in an anaerobic landfill leachate plume: II. Fate of aromatic and chlorinated aliphatic compounds. *J. Contamin. Hydrol.* **20**, 51–66.

Nielsen P. H., Bjerg P. L., Nielsen P., Smith P., and Christensen T. H. (1996) *In situ* and laboratory determined first-order degradation rate constants of specific organic compounds in an aerobic aquifer. *Environ. Sci. Technol.* **30**, 31–37.

Parkhurst D. L., Christenson S. C., and Breit G. N. (1993) *Ground-water Quality Assessment of the Central Oklahoma Aquifer, Oklahoma: Geochemical and Geohydrologic Investigations*. US Geological Survey Open File Report 92-642, US Geological Survey, Oklahoma City, OK.

Paxeus N. (2000) Organic compounds in municipal landfill leachates. *Water Sci. Technol.* **42**(7/8), 323–333.

Pecher K., Haderlein S. B., and Schwarzenbach R. P. (1997) Transformation of polyhalogenated alkanes in suspensions of ferrous iron and iron oxides. In *213th ASC National Meeting, April 13–17, 1997*. ASC Division of Environmental Chemistry, Washington, DC, pp. 185–187.

Petersen M. J. (2000) Modeling of groundwater flow and reactive transport in a landfill leachate plume. PhD Thesis, Department of Hydrodynamics and Hydraulic Engineering, Technical University of Denmark, Lyngby (ISVA Series Paper No. 73).

Postma D. (1993) The reactivity of iron oxides in sediments: a kinetic approach. *Geochim. Cosmochim. Acta* **57**, 5027–5034.

Ravi V., Chen J.-S., Wilson J. T., Johnson J. A., Gierke W., and Murdie L. (1998) Evaluation of natural attenuation of benzene and dichloroethane at the KL landfill. *Bioremed. J.* **2**, 239–258.

Reinhard M., Goodman N. L., and Barker J. F. (1984) Occurrence and distribution of organic chemicals in two landfill leachate plumes. *Environ. Sci. Technol.* **18**, 953–961.

Richnow H. H., Meckenstock R. U., Ask L., Baun A., Ledin A., and Christensen T. H. (2003) *In situ* biodegradation determined by carbon isotope fractionation of aromatic hydrocarbons in an anaerobic landfill leachate plume (Vejen, Denmark). *J. Contamin. Hydrol.* **64**, 59–72.

Rügge K., Bjerg P. L., and Christensen T. H. (1995) Distribution of organic compounds from municipal solid waste in the groundwater downgradient of a landfill (Grindsted, Denmark). *Environ. Sci. Technol.* **29**, 1395–1400.

Rügge K., Hofstetter T. B., Haderlein S. B., Bjerg P. L., Knudsen S., Zraunig C., Mosbæk H., and Christensen T. H. (1998) Characterization of predominant reductants in an anaerobic leachate-affected aquifer by nitroaromatic probe compounds. *Environ. Sci. Technol.* **32**, 23–31.

Rügge K., Bjerg P. L., Pedersen J. K., Mosbæk H., and Christensen T. H. (1999a) An anaerobic field injection experiment in a landfill leachate plume (Grindsted, Denmark): 1. Site description, experimental setup, tracer movement and fate of aromatic and chlorinated aliphatic compounds. *Water Resour. Res.* **35**, 1231–1246.

Rügge K., Bjerg P. L., Mosbæk H., and Christensen T. H. (1999b) Fate of MCPP and atrazine in an anaerobic landfill leachate plume (Grindsted, Denmark). *Water Res.* **33**, 2455–2458.

Röling W. F. M., van Breukelen B. M., Braster M., Groen J., and van Verseveld H. W. (2000) Analysis of microbial communities in a landfill leachate polluted aquifer using a new method for anaerobic physiological profiling and 16S rDNA based fingerprinting. *Microbiol. Ecol.* **40**, 177–188.

Röling W. F. M., van Breukelen B. M., Braster M., Lin B., and van Verseveld H. W. (2001) Relationship between microbial community structure and hydrochemistry in a landfill leachate-polluted aquifer. *Appl. Environ. Microbiol.* **67**, 4619–4629.

Scholl M. A. and Christenson S. C. (1998) *Spatial Variation in Hydraulic Conductivity Determined by Slug Tests in the Canadian River Alluvium near the Norman Landfill, Norman, Oklahoma*. US Geological Survey Water-Resources Investigations Report 97-4292, US Oklahoma City, OK.

Scholl M. A., Cozzarelli I. M., Christenson S. C., Breit G. N., and Schlottmann J. L. (1999) Aquifer heterogeneity at Norman Landfill and its effect on observations of biodegradation processes. In *US Geological Survey Toxic Substances Hydrology Program: Proceedings of the Technical Meeting, Charleston, South Carolina, March 8–12, 1999 Subsurface Contamination from Point Sources* (eds. D. W. Morganwalp and H. T. Buxton). US Geological Survey Water-Resources Investigations Report 99-4018C, West Trenton, NJ, vol. 3, pp. 557–568.

Scholl M. A., Cozzarelli I. M., Christenson S. C., Istok J., Jaeschke J., Ferree D. M., and Senko J. (2001) Measuring variability of *in-situ* biodegradation rates in a heterogeneous aquifer contaminated by landfill leachate. *EOS, Trans., AGU* **82**(20), 146.

Schwarzbauer J., Heim S., Brinker S., and Littke R. (2002) Occurrence and alteration of organic contaminants in seepage and leakage water from a waste deposit landfill. *Water Res.* **36**, 2275–2287.

Scott M. J. and Morgan J. J. (1990) Energetics and conservative properties of redox systems. *ACS Symp. Ser.* **416**, 368–378.

Senko J. M., Istok J. D., Suflita J. M., and Krumholz L. R. (2002) *In-situ* evidence for uranium immobilization and remobilization. *Environ. Sci. Technol.* **36**, 1491–1496.

Suarez M. P. and Rifai H. S. (1999) Biodegradation rates for fuel hydrocarbons and chlorinated solvents in groundwater. *Bioremed. J.* **3**, 337–362.

Sykes J. F., Soupak S., and Farquhar G. J. (1982) Modeling of leachate organic migration in groundwater below sanitary landfills. *Water Resour. Res.* **18**, 135–145.

Thornton S. F., Lerner D. N., and Banwart S. A. (2001) Assessing the natural attenuation of organic contaminants in aquifers using plume-scale electron carbon balances: model development with analysis and parameters sensitivity. *J. Contamin. Hydrol.* **53**, 199–232.

Tuxen N., Ejlskov P., Albrechtsen H.-J., Reitzel L. A., Pedersen J. K., and Bjerg P. L. Application of natural attenuation to ground water contaminated by phenoxy acid herbicides at an old landfill (Sjoelund, Denmark). *Ground Water Monit. R.* (in press).

Ulrich G. A., Martino D., Burger K., Routh J., Grossman E. L., Ammerman J. W., and Suflita J. M. (1998) Sulfur cycling in the terrestrial subsurface: commensal interactions, spatial scales, and microbial heterogeneity. *Microbiol. Ecol.* **36**, 141–151.

Ulrich G. A., Breit G. N., Cozzarelli I. M., and Suflita J. M. (2003) Sources of sulfate supporting anaerobic metabolism in a contaminated aquifer. *Environ. Sci. Technol.* **37**, 1093–1099.

van Duijvenbooden W. and Kooper W. F. (1981) Effects on groundwater flow and groundwater quality of a waste disposal site in Noordwijk, The Netherlands. *Quality of Groundwater: Proc. Int. Symp. Noordwijkerhout, March 1981*. Studies in Environmental Science,. Elsevier, Amsterdam, vol. 17, pp. 253–260.

Vogel T. M., Criddle C. S., and McCarty P. L. (1987) Transformations of halogenated aliphatic compounds. *Environ. Sci. Technol.* **21**, 722–736.